Synthesis, Stereochemistry and Molecular Structures of Chiral-at-Metal (Cycloheptatrienyl)molybdenum Complexes Containing the Diphosphane Prophos[‡]

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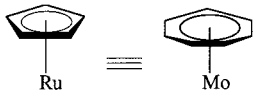
The synthesis of a series of 18-electron chiral-at-metal (cycloheptatrienyl)molybdenum complexes [(η^7-C_7H_7)Mo(prophos)X] [prophos = (*R*)-1,2-bis(diphenylphosphanyl)propane; X = $NCMeBF_4$, Cl, I, CN, H, Me] is reported, which consist of diastereomers differing only in the metal configuration. Diastereomer enrichments have been achieved and the configurational stability of the compounds [(η^7-C_7H_7)Mo(prophos)X] has been studied and compared with the isoelectronic ruthenium complexes [(η^5-C_5H_5)Ru(prophos)X]. The stereochemistry of the substitution reactions has been investigated, and X-ray analysis and NMR spectroscopy were used to determine the absolute configuration of the complexes.

Introduction

Cyclopentadienyl (η^5-C_5H_5) and benzene (η^6-C_6H_6) are among the most common ligands encountered in organotransition metal chemistry. Although transition metal complexes of the cycloheptatrienyl ligand η^7-C_7H_7 have been known for more than four decades, the chemistry of this ligand has not been studied much in comparison.[1] Until now, there is only one example of a chiral-at-metal cycloheptatrienyl complex.[2]

Whereas the neutral η^5-C_5H_5 ligand contributes 5 electrons to a metal centre, the (η^7-C_7H_7) ligand is a 7-electron ligand. As Ru has two electrons more than Mo, the isoelectronic fragments (η^5-C_5H_5)Ru and (η^7-C_7H_7)Mo should be intimately related (Scheme 1). The similarity of their chemistry will be corroborated in the present paper and in subsequent publications.[3,4]



Scheme 1

Three-legged "piano stool" complexes [(η^n-C_nH_n)MLL′L′′] are prominent examples of chiral-at-metal compounds.[5–7] Frequently, in these complexes the metal atom is the unique centre of chirality, with the compounds forming racemates. If one of the ligands is enantiomerically pure, a pair of diastereomers arises, differing only in the metal configuration. Usually, such diastereomers can be distinguished on the basis of their NMR spectra. Therefore, the diastereomer ratio and enrichment can be determined by the integration of suitable signals.

In solution some of the chiral-at-metal complexes are configurationally stable even at higher temperatures, whereas others are labile with respect to the metal configuration. Mostly, changes in the metal configuration are initiated by ligand dissociation, which converts an 18-electron species into an unsaturated 16-electron intermediate. Theoretical studies claim that for a series of isoelectronic 16-electron fragments [(η^n-C_nH_n)M(CO)$_2$] the ring size of the polyenyl ligand and the location of the metal in the periodic table have a distinct influence on the barrier of the pyramidal inversion at the metal centre.[8,9] The calculations showed that [(η^5-C_5H_5)Mn(CO)$_2$] and [(η^6-C_6H_6)Cr(CO)$_2$] have a pyramidal ground state and high inversion barriers. Interestingly, the situation changes upon going to either [(η^4-C_4H_4)Fe(CO)$_2$] or [(η^7-C_7H_7)V(CO)$_2$]. In both cases extremely shallow, only weakly pyramidal minima were found. As a consequence, [(η^5-C_5H_5)RuLL′L′′] and [(η^7-C_7H_7)MoLL′L′′] complexes should differ in their configurational stability, provided the change in the metal configuration includes a ligand dissociation.

In the present paper we compare the stereochemistry of the ruthenium complexes [(η^5-C_5H_5)Ru(prophos)X], studied by Consiglio et al.,[10] with the corresponding molybdenum compounds [(η^7-C_7H_7)Mo(prophos)X] (X = $NCMeBF_4$, Cl, I, CN, H, Me) (Scheme 2).[11]

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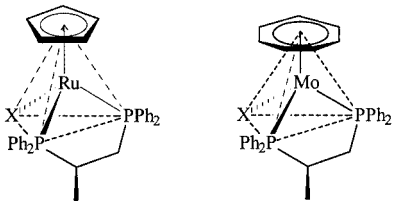
[‡‡] X-ray structure analyses.

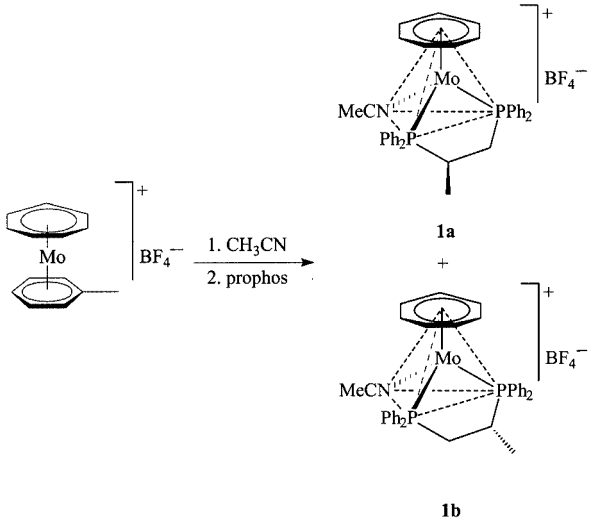


Scheme 2

Results and Discussion

1. Synthesis and Characterisation of Complexes 1a/1b

Reaction of the reactive complex $[(\eta^7\text{-}C_7H_7)Mo(\eta^6\text{-}C_6H_5CH_3)]BF_4$ [12] with the chiral diphosphane (*R*)-1,2-bis(diphenylphosphanyl)propane, (*R*)-prophos,[13] in CH_3CN resulted in the formation of a diastereomeric mixture $[(\eta^7\text{-}C_7H_7)Mo(prophos)(NCMe)]BF_4$ **1a/1b** (Scheme 3). The ratio of diastereomers could be determined by ^1H NMR spectroscopy as **1a/1b** = 93:7 in [D_6]acetone. It remained unchanged after 1 d in acetone solution. In the major diastereomer **1a**, the $\eta^7\text{-}C_7H_7$ signal was shifted to lower field compared to that of the minor diastereomer **1b**. Besides the C_7H_7 and the phenyl resonances, the ^1H NMR spectra of both diastereomers showed three signals due to the CH_2 and CH protons and a signal due to the methyl group of the diphosphane ligand, characterised by the expected coupling constants. The $^{31}P\{^1H\}$ NMR spectrum of the major diastereomer **1a** consisted of two doublets at δ = 71.7 and 56.1 ppm. The resonances of the minor diastereomer **1b** were shifted to δ = 76.1 and 62.7 ppm.



Scheme 3

Consiglio et al. had reported that in compounds of the type $[(\eta^5\text{-}C_5H_5)Ru(prophos)X]$ the major diastereomers having an (S_{Ru},R_C) configuration exhibited differences in the ^{31}P chemical shifts of the two phosphorus atoms P_A and P_B which were always larger than those of $P_{A'}$ and $P_{B'}$ of the (R_{Ru},R_C) diastereomers. Furthermore, the chemical shifts of the (R_{Ru},R_C) diastereomers usually fell between those of the (S_{Ru},R_C) diastereomers.[11] In keeping with such an empirical correlation, the absolute configuration of **1a/1b** was assigned on the basis of the ^{31}P chemical shifts of the molybdenum complexes **2**, **4**−**6** shown in Table 1. The absolute configurations of **2** and **4** are known from their X-ray structure determinations (see below), and those of **5** and **6** from NOE spectroscopy (see below). All 5 diastereomer pairs exhibit the same ^{31}P NMR pattern. Since the ^{31}P chemical shifts of the $P_{A'}$ and $P_{B'}$ signals of the minor (R_{Mo},R_C) diastereomers of **2b**, **4b**, **5b** and **6b** are larger than than those of P_A and P_B of the major (S_{Mo},R_C) diastereomers **2a**, **4a**, **5a** and **6a**, we assign an (R_{Mo},R_C) configuration to **1b** and an (S_{Mo},R_C) configuration to **1a**.

Table 1. ^{31}P chemical shifts for the two phosphorus atoms in the molybdenum complexes **1**, **2**, **4**, **5**, **6**

Complex (solvent)	P_A [ppm]	$P_{A'}$ [ppm]	P_B [ppm]	$P_{B'}$ [ppm]
1 ([D_6]acetone)	71.7	76.1	56.1	62.7
2 (C_6D_6)	65.5	65.8	51.1	56.1
4 (C_6D_6)	69.7	74.3	53.9	61.8
5 (C_6D_6)	81.1	86.3	64.1	68.3
6 (C_6D_6)	77.6	77.4	60.0	64.0

The CH_3CN ligand in $[(\eta^7\text{-}C_7H_7)Mo(prophos)(NCMe)]BF_4$ (**1**) proved to be substitutionally labile. It could be replaced by CD_3CN (20 equiv.) in a solution of **1** in [D_6]acetone at room temperature [Equation (1)].

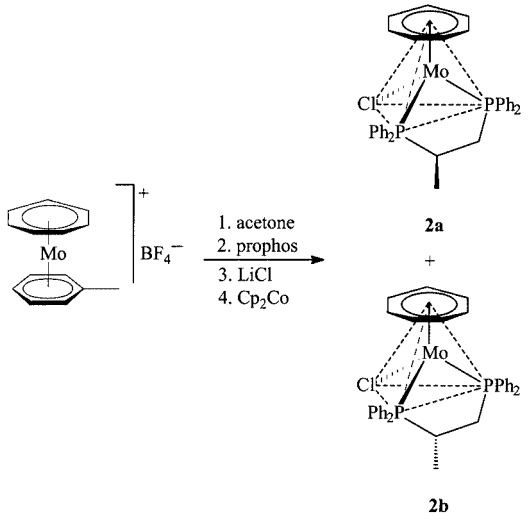
$$[(\eta^7\text{-}C_7H_7)Mo(prophos)(CH_3CN)]BF_4 + CD_3CN \rightarrow [(\eta^7\text{-}C_7H_7)Mo(prophos)(CD_3CN)]BF_4 + CH_3CN \quad (1)$$

The kinetics of this process was studied by ^1H NMR spectroscopy and analysed for pseudo-first-order conditions. The first-order rate constant obtained was $1.86 \cdot 10^{-3}$ min^{-1} at 21.8 °C (half-life 373 min). During the exchange no significant change in the diastereomeric ratio was observed. In comparison to the related ruthenium complex $[(\eta^5\text{-}C_5H_5)Ru(ppfa)(NCMe)]PF_6$ {ppfa = 2-[1-(dimethylamino)ethyl]-1-(diphenylphosphanyl)ferrocene}, the CH_3CN exchange in **1** was considerably slower.[14]

2. Synthesis and Characterisation of Complexes 2a/2b

Treatment of $[(\eta^7\text{-}C_7H_7)Mo(\eta^6\text{-}C_6H_5CH_3)]BF_4$ in acetone with 1 equiv. of (*R*)-prophos caused displacement of the $(\eta^6\text{-}C_6H_5CH_3)$ ligand. Reaction with an excess of anhydrous LiCl afforded the 17-electron cation $[(\eta^7\text{-}C_7H_7)Mo(prophos)Cl]^+$. The synthesis of the neutral 18-electron diastereomers $[(\eta^7\text{-}C_7H_7)Mo(prophos)Cl]$ (**2a/2b**) from the radical cation in $[(\eta^7\text{-}C_7H_7)Mo(prophos)Cl]BF_4$ was achieved by reduction with $CoCp_2$ in toluene (Scheme 4).[15−17] The complexes **2a/2b** initially failed to give satisfactory NMR spectra, probably due to trace oxidation. However, good NMR spectroscopic data for **2a/2b** were obtained on addition of a small quantity of $CoCp_2$ to the sample.[18] The diastereomer ratio could be determined

by ^{1}H NMR spectroscopy as **2a/2b** = 82:18 in C_6D_6. It remained unchanged after 1 d in benzene solution. In the major diastereomer **2a**, the η^7-C_7H_7 signal was shifted to



Scheme 4

lower field compared to that of the minor diastereomer **2b**.

Consiglio et al. had found in their studies, that the chiral-at-metal complex [(η^5-C_5H_5)Ru(prophos)Cl] was configurationally stable at room temperature and even did not epimerise in benzene at 80 °C.[19] In contrast, the analogous molybdenum complex [(η^7-C_7H_7)Mo(prophos)Cl] (**2**) epimerised at higher temperatures at the metal centre with no apparent decomposition. Thus, an 82:18 mixture of **2a/2b** changed to 90:10 after 18 h and to 93:7 after 42 h at 60 °C in C_6D_6. This result confirms the theoretical studies[8,9] that had predicted a lower barrier of the pyramidal inversion for (η^7-C_7H_7)MoLL systems compared to (η^5-C_5H_5)RuLL systems.

3. Molecular Structure of Diastereomer 2a

To determine the absolute configuration of the major diastereomer [(η^7-C_7H_7)Mo(prophos)Cl] (**2a**) by X-ray analysis, single crystals were grown in CH_2Cl_2/hexane from a 93:7 mixture of **2a/2b**. The molecular structure of **2a** is depicted in Figure 1 and selected structural parameters are listed in Table 2.

The η^7-C_7H_7 ring occupies three *fac* positions of an octahedral metal environment, which is completed by the chelate phosphane group and a terminal chlorine atom. The absolute configuration of the metal centre is (S_{Mo}) in agreement with the ligand priority sequence[20,21] η^7-C_7H_7 > Cl > P1(CH_3) > P2. Thus, the thermodynamically more stable diastereomer **2a** has (S_{Mo},R_C) configuration.

The cycloheptatrienyl ring is almost planar. The molybdenum atom lies 1.612 Å apart from the least-squares plane through the carbocyclic ring. The two Mo−P bond lengths are slightly different from each other. The sequence of the angles around the molybdenum atom is P1−Mo1−P2 < P1−Mo1−Cl1 < P2−Mo1−Cl1, with the chlorine ligand displaced towards P1.

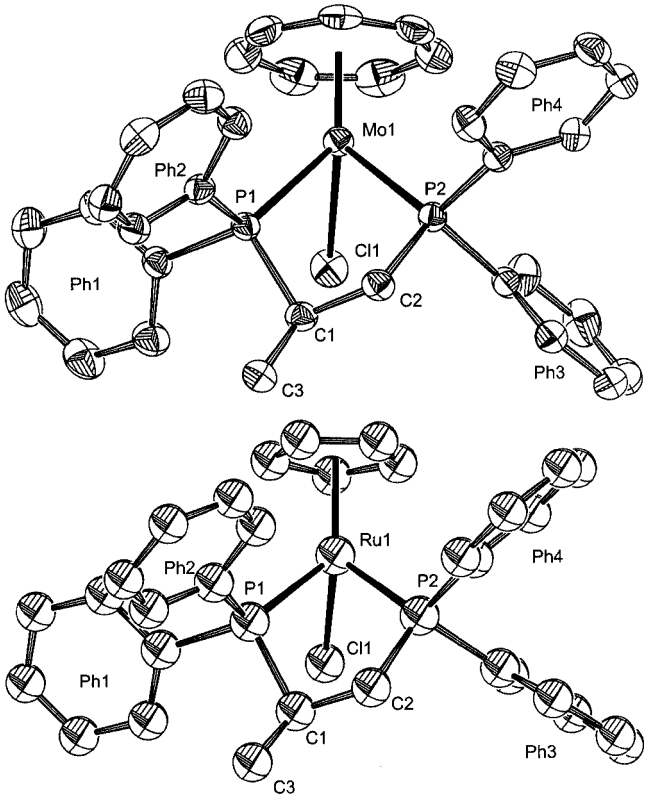


Figure 1. Molecular structures of (S_{Mo},R_C)-[(η^7-C_7H_7)Mo(prophos)Cl] (**2a**) (top) and (S_{Ru},R_C)-[(η^5-C_5H_5)Ru(prophos)Cl][20] (bottom); hydrogen atoms have been omitted for clarity

As compound (S_{Mo},R_C)-[(η^7-C_7H_7)Mo(prophos)Cl] (**2a**) resembles the complex (S_{Ru},R_C)-[(η^5-C_5H_5)Ru(prophos)Cl],[19] it was interesting to compare their molecular structures (Figure 1). The similarity is striking. In both complexes even the phenyl rings (except Ph4) of the prophos ligand are orientated in the same way. As a consequence of the smaller polyenyl ligand, the bond C(g)−Ru (1.851 Å) in [(η^5-C_5H_5)Ru(prophos)Cl] is longer than the bond C(g)−Mo (1.612 Å) in **2a** [C(g) = ring centroid]. Due to the different metal radii, the M−P bonds are about 0.2 Å shorter in the ruthenium complex.

The Mo(prophos) metallacycle in [(η^7-C_7H_7)Mo(prophos)Cl] (**2a**) has λ conformation allowing an equatorial disposition of the methyl group C3 of the (*R*)-prophos ligand. The two carbon atoms C1 and C2 of the five-membered ring are both on the same side of the P1−Mo1−P2 plane, a frequently found conformation (distorted envelope conformation).[22] The Ru(prophos) metallacycle in [(η^5-C_5H_5)Ru(prophos)Cl] also has λ conformation with a torsion angle P2−C2−C1−P1 of −43.77°, which is smaller than the analogous angle in **2a** of −53.21° (Figure 2).

4. Synthesis and Characterization of Complexes 3a/b and 4a/b

Reaction of [(η^7-C_7H_7)Mo(prophos)(NCMe)]BF_4 (**1**) with an excess of NaI in acetone afforded the 18-electron complex [(η^7-C_7H_7)Mo(prophos)I] (**3**) (Scheme 5). The dia-

Table 2. Selected bond lengths [Å] and angles [°] for compounds [(η^n-C_nH_n)M(prophos)X]: [(η^5-C_5H_5)Ru(prophos)Cl],[19] [(η^7-C_7H_7)Mo(prophos)Cl] (**2a**), -[(η^7-C_7H_7)Mo(prophos)I] (**3a**) and [(η^7-C_7H_7)Mo(prophos)CN] (**4a**)

Complex	[CpRu(prophos)Cl]	**2a**	**3a**	**4a**
Stereochemistry	(S_{Ru},R_C)	(S_{Mo},R_C)	(R_{Mo},R_C)	(S_{Mo},R_C)
X	Cl	Cl	I	CN
M−P1	2.278(2)	2.4898(5)	2.5152(7)	2.4740(18)
M−P2	2.276(2)	2.4692(6)	2.4801(7)	2.4551(17)
M−X	2.444(2)	2.5355(5)	2.8774(3)	2.116(9)
M−C(g)[a]	1.851	1.612	1.621	1.626
P1−M−P2	82.9(1)	78.14(2)	78.04(2)	78.79(5)
P1−M−X	84.0(1)	78.86(2)	80.72(2)	78.61(19)
P2−M−X	92.9(1)	86.77(2)	89.62(2)	85.36(19)
P2−C2−C1−P1	−43.77	−53.21(15)	−52.75(19)	−51.5(5)
P1−M−P2−C2	10.8	−0.67(6)	−0.70(9)	−0.5(2)
P2−M−P1−C1	−29.9	−24.68(7)	−24.35(8)	−24.1(2)

[a] C(g) indicates the centre of the polyenyl ligand.

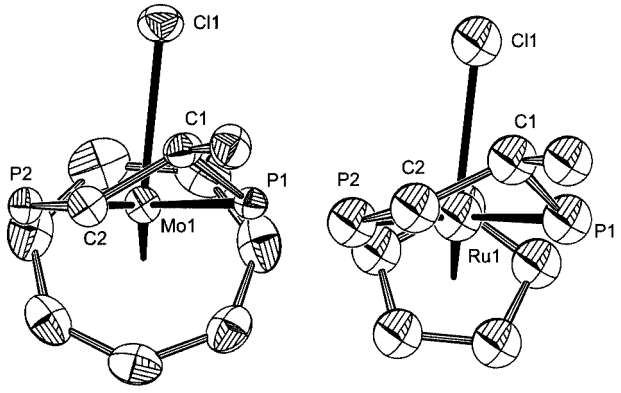
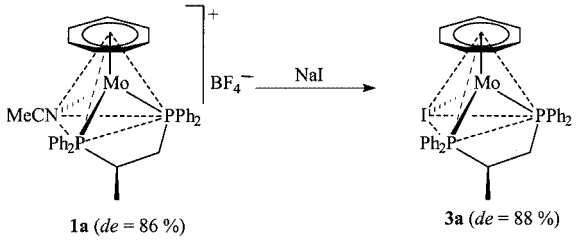


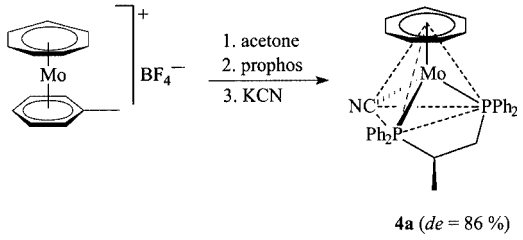
Figure 2. (S_{Mo},R_C)-[(η^7-C_7H_7)Mo(prophos)Cl] (**2a**) (left) and (S_{Ru},R_C)-[(η^5-C_5H_5)Ru(prophos)Cl] (right); view along the plane P1−M−P2 that is normal to the plane of the drawing, showing the λ conformation of the M(prophos) ring and the equatorial arrangement of the methyl group of prophos

stereomer ratio could be determined by ^{1}H NMR spectroscopy as **3a/3b** = 94:6 in C_6D_6. It remained unchanged after 1 d in benzene solution. By fractional crystallisation it was possible to increase the diastereomer ratio to 98:2. After 3 h at 70 °C in benzene solution, the diastereomer ratio changed to 94:6. Thus, analogous to complex **2**, compound [(η^7-C_7H_7)Mo(prophos)I] (**3**) epimerised at higher temperatures in solution. Interestingly, the variation of the halogen had no considerable influence on the equilibrium ratio.



Scheme 5

The cyano complex [(η^7-C_7H_7)Mo(prophos)(CN)] (**4a/4b**) was obtained from the reaction of [(η^7-C_7H_7)Mo(prophos)($OCMe_2$)]BF_4 with KCN in acetone/methanol (Scheme 6). It was isolated as a red solid after purification by column chromatography. The diastereomer ratio could be determined by ^{1}H NMR spectroscopy as **4a/4b** = 93:7 in $CDCl_3$. This ratio remained unchanged after 1 d in $CDCl_3$ solution.



Scheme 6

5. Molecular Structures of Complexes 3a and 4a

Single crystals of [(η^7-C_7H_7)Mo(prophos)I] (**3a**) were grown at room temp. from toluene/pentane using a **3a/3b** = 98:2 mixture. An ORTEP view of **3a** is shown in Figure 3. The structure determination confirmed the (R_C) configuration of the stereogenic carbon centre. The configuration of the molybdenum centre was specified as (R_{Mo}) using the priority sequence I > η^7-C_7H_7 > P1(CH_3) > P2.

There is a change in the priority sequence of the ligands in **3a** and **2a**. Thus, (R_{Mo},R_C)-[(η^7-C_7H_7)Mo(prophos)I] (**3a**) and (S_{Mo},R_C)-[(η^7-C_7H_7)Mo(prophos)Cl] (**2a**) have opposite descriptors for the chiral metal atoms, although they have the same relative configuration (Figure 1 and Figure 3). The structural parameters of **3a** are very similar to those of **2a** except for the Mo−Hal part (Table 2). The cycloheptatrienyl ligand in **3a** is roughly planar with slightly different C−C [range 1.398(5)−1.417(4) Å] and Mo−C bond lengths, a consequence of the asymmetry of the coordination around the metal centre.

To determine the absolute configuration of the major diastereomer [(η^7-C_7H_7)Mo(prophos)CN] (**4a**) by X-ray analysis, single crystals were grown in $CHCl_3$/pentane from a

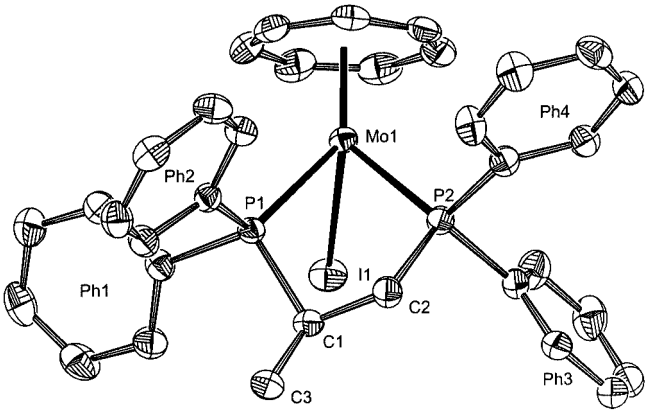


Figure 3. Molecular structure of (R_{Mo},R_C)-[(η^7-C_7H_7)Mo(prophos)I] (**3a**) (hydrogen atoms omitted for clarity)

93:7 mixture of **4a/4b**. The molecular structure of **4a** is shown in Figure 4. It has an (S_{Mo},R_C) configuration which relates it to the relative configuration of **2a** and **3a**.

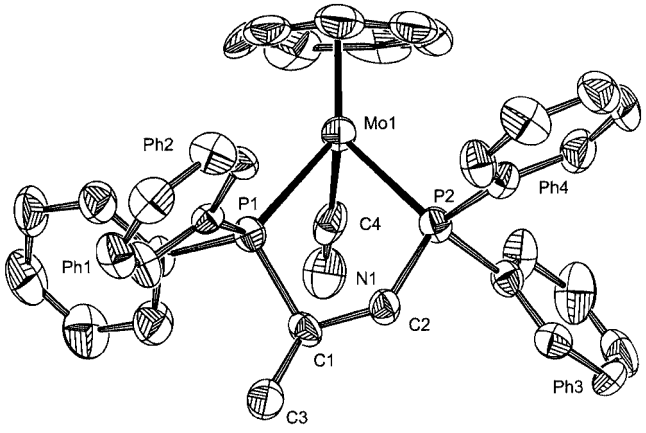
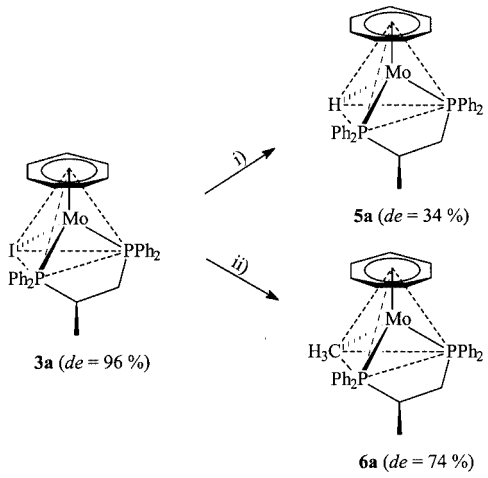


Figure 4. Molecular structure of (S_{Mo},R_C)-[(η^7-C_7H_7)Mo(prophos)CN] (**4a**) (hydrogen atoms omitted for clarity)

6. Formation of the Complexes 5a/b and 6a/b

Starting from [(η^7-C_7H_7)Mo(prophos)I] with a diastereomer ratio of **3a/3b** = 98:2 the reduction with sodium dihydrobis(2-methoxyethoxy)aluminate gave the hydrido compound [(η^7-C_7H_7)Mo(prophos)H] (**5a/5b**) (Scheme 7). The diastereomer ratio of the product could be determined by ^{1}H NMR spectroscopy as **5a/5b** = 67:33 in C_6D_6. The same ratio was obtained starting from [(η^7-C_7H_7)Mo(prophos)Cl] with a diastereomer ratio of **2a/2b** = 82:18. These results indicate that the metal centre in [(η^7-C_7H_7)Mo(prophos)H] **5a/5b** is configurationally labile. Obviously, the 67:33 mixture is the equilibrium ratio for **5a/5b**.

Complex [(η^7-C_7H_7)Mo(prophos)Me] (**6a/6b**) was prepared by reaction of [(η^7-C_7H_7)Mo(prophos)I] with MeLi in THF at 30 °C. The diastereomer ratio of the product could be determined as **6a**:**6b** = 87:13 in C_6D_6. This ratio remained unchanged after 1 d at 21 °C in solution. At higher temperatures decomposition occurred. By contrast,



Scheme 7. i) $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ in toluene; ii) MeLi in THF

reaction of [(η^5-C_5H_5)Ru(prophos)Cl] at room temperature in toluene with an ether solution of CH_3MgBr stereospecifically had given the corresponding methyl derivative [(η^5-C_5H_5)Ru(prophos)Me] and reaction of [(η^5-C_5H_5)Ru(prophos)Cl] with methanolic CH_3ONa leading to the hydride [(η^5-C_5H_5)Ru(prophos)H] took place with retention of configuration at the ruthenium atom.[23]

As it was not possible to obtain single crystals of **5** and **6** for an X-ray analysis, the stereochemical assignment of **5** and **6** was accomplished by NOE experiments.[11] The thermodynamically more stable diastereomers were the (S_{Mo},R_C) epimers **5a** and **6a**. The determination of the absolute configuration at the chiral molybdenum atom was based on the NOEs between R (**5a**, R = H; **6a**, R = Me) and the hydrogen atom H_g bound to the chiral carbon atom of the diphosphane. The assignment of the *ortho* proton resonances for the four phenyl groups was made by inspection of their NOEs with R, H_g, H_c, H_t and the Me group of the diphosphane ligand. These NOEs supported an equatorial disposition of the methyl group in **5a** and **6a** with a λ conformation of the Mo(prophos) metallacycle (Figure 5).

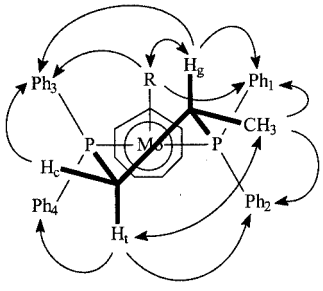


Figure 5. Schematic view of the prophos ligand in (S_{Mo},R_C)-[(η^7-C_7H_7)Mo(prophos)H] (**5a**) (R = H) and (S_{Mo},R_C)-[(η^7-C_7H_7)Mo(prophos)Me] (**6a**) (R = Me) projected onto the C_7H_7 ring; some selected NOEs are shown

Conclusions

The new (η^7-C_7H_7)Mo complexes described in this paper are isolobal with the corresponding (η^5-C_5H_5)Ru complexes investigated by Consiglio et al.[10,19,23] Whereas [(η^7-C_7H_7)Mo(prophos)Cl] undergoes epimerization in solution at temperatures around 60 °C, [(η^5-C_5H_5)Ru(prophos)Cl] is configurationally stable at this temperature. In contrast to the analogous ruthenium complexes, the formation of [(η^7-C_7H_7)Mo(prophos)H] and [(η^7-C_7H_7)Mo(prophos)Me] was not stereospecific. Thus, our investigations demonstrate that the new (η^7-C_7H_7)Mo complexes are configurationally more labile at the metal centre than their (η^5-C_5H_5)Ru counterparts.

Experimental Section

General Remarks: All manipulations were carried out under dry nitrogen using standard Schlenk techniques. Most of the commercially available reagents were used without further purification. Solvents were dried by standard methods and distilled prior to use. Melting points (not corrected): Büchi SMP 20. IR spectra: BioRad FT-IR (KBr pellets). Mass spectra: Finnigan Mat 311 A, Finnigan Mat 95 and ThermoQuest TSQ 7000. Optical rotations: Perkin−Elmer 241 polarimeter at room temperature. ^{1}H NMR spectra: Bruker ARX 400 spectrometer (400 MHz). ^{31}P NMR spectra: Bruker ARX 400 spectrometer (162 MHz). Elemental analyses: Heraeus Elementar Vario El III. The diphosphane (*R*)-prophos[13] and the complex [(η^7-C_7H_7)Mo(η^6-$C_6H_5CH_3$)]BF_4 [12] were prepared according to the literature.

[(η^7-C_7H_7)Mo(prophos)(NCMe)]BF_4 (1): A solution of [(η^7-C_7H_7)Mo(η^6-$C_6H_5CH_3$)]BF_4 (0.190 g, 0.47 mmol) was refluxed in CH_3CN for 1 h. The red solution was cooled to 0 °C, treated with prophos (0.185 g, 0.45 mmol) and refluxed for 3 h. The resulting solution was filtered and the volume was reduced to ca. 5 mL. Addition of diethyl ether precipitated **1** as a pink solid. Yield 298 mg (91%). M.p. 209 °C. IR (KBr): $\tilde{\nu}$ = 3060 w, 2990 w, 2970 w, 1490 m, 1440 s, 1070 s, 830 m, 750 m, 710 m cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]acetone; signal of the minor diastereomer in parentheses): δ = 7.73−7.13 (m, 20 H, Ph-*H*), 5.09 (4.88) (dd, J_{HP} = 2.2 Hz, J_{HP} = 2.1 Hz, 7 H, η^7-C_7H_7), 2.99 (dddd, J_{HP} = 48.9, $^2J_{H,H}$ = 14.9 Hz, J_{HP} = 12.6, $^3J_{H,H}$ = 4.3 Hz, 1 H, CH_AH$_B$), 2.15 (m, 1 H, C*H*CH$_3$), 1.87 (dddd, $^2J_{H,H}$ = 14.9, $^3J_{H,H}$ = 14.9 Hz, J_{HP} = 6.4 Hz, J_{HP} = 2.5 Hz, 1 H, CH$_A$*H*$_B$), 1.63 (dd, J_{HP} = 1.6 Hz, J_{HP} = 1.6 Hz, 3 H, NCC*H*$_3$), 0.97 (ddd, J_{HP} = 10.4, $^3J_{H,H}$ = 6.6 Hz, J_{HP} = 1.2 Hz, 3 H, CHC*H*$_3$) ppm. ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]acetone; signal of the minor diastereomer in parentheses): δ = 71.7 (76.1) (d, J_{PP} = 23.7 Hz), 56.1 (62.7) (d) ppm. MS (FAB-MS): *m*/*z* (%) = 642 (15) [cation], 601 (100) [cation − NCMe]. [α]$_D$ = +10, [α]$_{578}$ = −20, [α]$_{546}$ = −170, [α]$_{436}$ = −600 (*c* = 0.16, acetone). $C_{36}H_{36}BF_4MoNP_2$ (727.38): calcd. C 59.45, H 4.99, N 1.93; found C 58.42, H 4.97, N 1.94.

[(η^7-C_7H_7)Mo(prophos)Cl] (2): A solution of [(η^7-C_7H_7)Mo(η^6-$C_6H_5CH_3$)]BF_4 (0.150 g, 0.41 mmol) and prophos (0.170 g, 0.41 mmol) was stirred in acetone for 20 h. Then the solution was treated with LiCl (0.250 g, 5.9 mmol) and stirred for 20 h. The solvent was removed and the residue was washed with toluene and dried; 0.180 g of the green solid was suspended in toluene and treated with Cp_2Co (0.047 g, 0.25 mmol). The mixture was stirred at 35 °C. After 3 h, the solution was filtered and the solvent was removed. Recrystallisation of the crude product from CH_2Cl_2/hexane gave **2** as a green solid. Yield 80 mg (30%). M.p. > 250 °C. IR (KBr): $\tilde{\nu}$ = 3060 w, 2990 w, 2970 w, 1490 m, 1440 s, 1100 m, 820 m, 740 m, 690 m cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6; signal of the minor diastereomer in parentheses): δ = 8.01−7.90 (m, 2 H, Ph-*H*), 7.65−7.47 (m, 2 H, Ph-*H*), 7.37−6.92 (m, 16 H, Ph-*H*), 4.86 (4.79) (dd, J_{HP} = 1.9 Hz, J_{HP} = 1.9 Hz, 7 H, η^7-C_7H_7), 2.62 (m, 1 H, C*H*CH$_3$), 2.09 (dddd, J_{HP} = 46.7, $^2J_{H,H}$ = 14.7 Hz, J_{HP} = 10.9, $^3J_{H,H}$ = 5.2 Hz, 1 H, CH_AH$_B$), 1.38 (dddd, $^2J_{H,H}$ = 14.7, $^3J_{H,H}$ = 14.5 Hz, J_{HP} = 6.4 Hz, J_{HP} = 2.5 Hz, 1 H, CH$_A$*H*$_B$), 0.62 (0.76) (ddd, J_{HP} = 9.4, $^3J_{H,H}$ = 6.8 Hz, J_{HP} = 1.1 Hz, 3 H, CHC*H*$_3$) ppm. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6; signal of the minor diastereomer in parentheses): δ = 65.5 (65.8) (d, J_{PP} = 16.0 Hz), 51.1 (56.1) (d) ppm. MS (FD-MS, CH_2Cl_2): *m*/*z* (%) = 636 (100) [M$^+$]. [α]$_D$ = −860, [α]$_{578}$ = −890, [α]$_{546}$ = −660 (*c* = 0.12, CH_2Cl_2). $C_{34}H_{33}ClMoP_2$ (634.98): calcd. C 64.31, H 5.24; found C 63.87, H 5.35.

[(η^7-C_7H_7)Mo(prophos)I] (3): Compound **1** (0.235 g, 0.32 mmol) in 30 mL of acetone was treated with NaI (0.200 g, 1.33 mmol). The reaction mixture was stirred for 20 h at room temp. and 3 h at 40 °C. The solvent was then removed and the residue was extracted with toluene (60 mL). The solution was filtered and reduced in volume. Addition of pentane gave green needles of **3**, which were dried in vacuo. Yield 181 mg (78%). M.p. > 250 °C. IR (KBr): $\tilde{\nu}$ = 3048 w, 2978 w, 2923 w, 2869 w, 1482 m, 1434 s, 1093 m, 814 s, 742 s, 696 s, 518 s cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6; signal of the minor diastereomer in parentheses): δ = 7.97−7.90 (m, 2 H, Ph-*H*), 7.63−7.57 (m, 2 H, Ph-*H*), 7.48−7.42 (m, 2 H, Ph-*H*), 7.33−7.21 (m, 5 H, Ph-*H*), 7.20−7.02 (m, 9 H, Ph-*H*), 4.88 (4.82) (dd, J_{HP} = 1.9 Hz, J_{HP} = 1.9 Hz, 7 H, η^7-C_7H_7), 2.99 (m, 1 H, C*H*CH$_3$), 2.23 (dddd, J_{HP} = 46.4, $^2J_{H,H}$ = 14.7 Hz, J_{HP} = 10.7, $^3J_{H,H}$ = 5.5 Hz, 1 H, CH_AH$_B$), 1.32 (dddd, $^2J_{H,H}$ = 14.7, $^3J_{H,H}$ = 14.5 Hz, J_{HP} = 5.2 Hz, J_{HP} = 4.9 Hz, 1 H, CH$_A$*H*$_B$), 0.65 (0.97) (ddd, J_{HP} = 9.6, $^3J_{H,H}$ = 6.8 Hz, J_{HP} = 1.4 Hz, 3 H, CHC*H*$_3$) ppm. MS (FD-MS, CH_2Cl_2): *m*/*z* (%) = 728 (100) [M$^+$]. [α]$_D$ = −750, [α]$_{578}$ = −790, [α]$_{546}$ = −670, [α]$_{436}$ = −1500 (*c* = 0.16, CH_2Cl_2). $C_{34}H_{33}IMoP_2$ (726.43): calcd. C 56.22, H 4.58; found C 55.84, H 4.70.

[(η^7-C_7H_7)Mo(prophos)CN] (4): A solution of [(η^7-C_7H_7)Mo(η^6-$C_6H_5CH_3$)]BF_4 (0.364 g, 1.00 mmol) and prophos (0.412 g, 1.00 mmol) in 40 mL of acetone was refluxed for 18 h. The solution was reduced in volume to 10 mL and methanol (30 mL) was added. The resulting solution was treated with KCN and stirred for 30 min at 50 °C. The solvent was removed and the residue was extracted with CH_2Cl_2 (20 mL). The mixture was filtered through a plug of Al_2O_3 and the solvents were evaporated to dryness. The resulting solid was dissolved in CH_2Cl_2 and transferred to an Al_2O_3/hexane chromatography column cooled to 10 °C. Elution with acetone/hexane gave a red band, which was collected and the solvents were evaporated to dryness. Crystallisation of the crude product from $CHCl_3$/pentane gave **4** as red plates. Yield 199 mg (32%). M.p. > 250 °C. IR (KBr): $\tilde{\nu}$ = 3050 w, 2980 w, 2920 w, 2860 w, 2070 s, 1440 s, 1100 m, 820 m, 740 m, 690 m cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$; signal of the minor diastereomer in parentheses): δ = 7.83−6.95 (m, 20 H, Ph-*H*), 4.70 (4.54) (dd, J_{HP} = 2.2 Hz, J_{HP} = 2.2 Hz, 7 H, η^7-C_7H_7), 2.68−2.54 (m, 1 H, C*H*CH$_3$), 2.40 (dddd, J_{HP} = 48.1, $^2J_{H,H}$ = 14.7 Hz, J_{HP} = 11.7, $^3J_{H,H}$ = 5.1 Hz, 1 H, CH_AH$_B$), 1.52 (dddd, $^2J_{H,H}$ = 14.7, $^3J_{H,H}$ = 14.5 Hz, J_{HP} = 6.4 Hz, J_{HP} = 4.3 Hz, 1 H, CH$_A$*H*$_B$), 0.84 (0.75) (ddd, J_{HP} = 8.8, $^3J_{H,H}$ = 7.8 Hz, J_{HP} = 1.3 Hz, 3 H, CHC*H*$_3$) ppm. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6; signal of the minor diastereomer in parentheses): δ = 69.7 (74.3) (d, J_{PP} = 26.7 Hz), 53.9 (61.8) (d) ppm. MS (FD-MS, CH_2Cl_2): *m*/*z* (%) = 627 (100) [M$^+$]. $C_{35}H_{33}MoNP_2$ (625.54): calcd. C 67.20, H 5.32, N 2.24; found C 66.12, H 5.95, N 1.84.

[(η⁷-C_7H_7)Mo(prophos)H] (5): Compound [(η⁷-C_7H_7)Mo(prophos)I] (**3**) (60.0 mg, 0.83 μmol) was dissolved in 15 mL of toluene. To this solution was added RedAl© (80 μL of a 70% solution in toluene) at −20 °C. The mixture was stirred for 16 h at room temp. and then for 10 h at 30 °C. After cooling to 0 °C, water (0.1 mL) was added and the solvent was removed. The residue was extracted with toluene (5 mL). The mixture was filtered and the solvents were evaporated to dryness. Yield 32 mg (68%). ^{1}H NMR (400 MHz, C_6D_6; signal of the minor diastereomer in parentheses): δ = 8.07−6.90 (m, 20 H, Ph-*H*), 4.78 (4.72) (ddd, J_{HP} = 1.9 Hz, J_{HP} = 1.9 Hz, $J_{H,H}$ = 1.3 Hz, 7 H, η⁷-C_7H_7), 2.11 (dddd, J_{HP} = 50.1, $^2J_{H,H}$ = 13.7 Hz, J_{HP} = 10.0, $^3J_{H,H}$ = 4.4 Hz, 1 H, CH_AH$_B$), 2.03−1.87 (m, 1 H, C*H*CH$_3$), 1.60 (dddd, $^3J_{H,H}$ = 13.8, $^2J_{H,H}$ = 13.7 Hz, J_{HP} = 6.7 Hz, J_{HP} = 3.1 Hz, 1 H, CH$_A$$H_B$), 0.72 (0.66) (dd, J_{HP} = 9.4, $^3J_{H,H}$ = 6.8 Hz, 3 H, CHCH_3), −4.07 (−3.58) (dd, J_{HP} = 59.1 Hz, J_{HP} = 41.7 Hz, 1 H, Mo-*H*) ppm. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6; signal of the minor diastereomer in parentheses): δ = 81.1 (86.3) (d, J_{PP} = 25.2 Hz), 64.1 (68.3) (d).

[(η⁷-C_7H_7)Mo(prophos)Me] (6): Methyllithium (0.8 mL of a 1.6 M solution in diethyl ether) was added to [(η⁷-C_7H_7)Mo(prophos)I] (**3**) (60.0 mg, 83 μmol) in THF (16 mL) at −78 °C. The solution was warmed to 0 °C and stirred for 3 h at this temperature. After 30 min at room temp., the solvent was removed. The residue was filtered through a plug of Celite® and the solvents were evaporated. The resulting solid was dissolved in hexane and transferred to a cooled Al_2O_3/hexane chromatography column maintained at −78 °C. Elution with hexane gave a red band, which was collected and the solvents were evaporated to dryness. Yield 49 mg (78%). ^{1}H NMR (400 MHz, C_6D_6; signal of the minor diastereomer in parentheses): δ = 7.79−6.94 (m, 20 H, Ph-*H*), 4.67 (4.66) (dd, J_{HP} = 1.9 Hz, J_{HP} = 1.9 Hz, 7 H, η⁷-C_7H_7), 2.28 (dddd, J_{HP} = 48.0, $^2J_{H,H}$ = 14.5 Hz, J_{HP} = 10.9, $^3J_{H,H}$ = 4.8 Hz, 1 H, CH_AH$_B$), 2.04−1.89 (m, 1 H, C*H*CH$_3$), 1.56 (dddd, $^3J_{H,H}$ = 14.7, $^2J_{H,H}$ = 14.5 Hz, J_{HP} = 6.0 Hz, J_{HP} = 3.3 Hz, 1 H, CH$_A$$H_B$), 0.66 (0.88) (ddd, J_{HP} = 9.0, $^3J_{H,H}$ = 6.7 Hz, J_{HP} = 1.0 Hz, 3 H, CHCH_3), −0.66 (−0.42) (dd, J_{HP} = 8.6 Hz, J_{HP} = 6.8 Hz, 3 H, CH_3) ppm. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6; signal of the minor diastereomer in parentheses): δ = 77.6 (77.4) (d, J_{PP} = 17.2 Hz), 60.0 (64.0) (d).

Acetonitrile Exchange Kinetics with 1 in [D$_6$]Acetone: The CH_3CN exchange in **1** was studied by monitoring the decrease in intensity of the ^{1}H NMR signal of the coordinated [CH_3CN]$_c$ (at δ = 1.63 ppm) and the increase of the free [CH_3CN]$_f$ (at δ = 2.05 ppm) after injection of CD_3CN. After adjusting to the selected temperature, the deuterated acetonitrile was added and spectra were taken at regular intervals. The time dependence of the mol fraction x = [CH_3CN]$_c$/([CH_3CN]$_c$ + [CH_3CN]$_f$), obtained by integration of the corresponding signals, was fitted to Equation (2),[14,24] in which x_0 and x_∞ are the values of x at t = 0 and ∞, and k is the observed first-order rate constant for the exchange.

$$x = x_\infty + (x_0 - x_\infty)\exp[-kt/(1 - x_\infty)] \quad (2)$$

Table 3. Crystal data, data collection and structure refinement for [(η⁷-C_7H_7)Mo(prophos)Cl] (**2a**), [(η⁷-C_7H_7)Mo(prophos)I] (**3a**), and [(η⁷-C_7H_7)Mo(prophos)CN] (**4a**)

	2a	**3a**	**4a**
Empirical formula	$C_{34}H_{33}ClMoP_2$	$C_{34}H_{33}IMoP_2$	$C_{35}H_{33}MoNP_2$
Formula mass	634.98	726.43	625.54
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
Radiation	Mo-K_α	Mo-K_α	Cu-K_α
Z	4	4	4
Unit cell dimensions	a = 11.4591(8) Å	a = 11.7172(6) Å	a = 11.5122(8) Å
	b = 15.5525(10) Å	b = 15.6560(8) Å	b = 15.6901(15) Å
	c = 16.5821(15) Å	c = 16.4373(11) Å	c = 16.6296 (19) Å
Cell volume	2955.2(4) Å^3	3015.3(3) Å^3	3003.8(5) Å^3
Density (calculated)	1.427 g/cm^3	1.600 g/cm^3	1.383 g/cm^3
Absorption coefficient	0.66 mm^{-1}	1.587 mm^{-1}	4.75 mm^{-1}
F(000)	1304	1448	1288
Crystal size	0.48 × 0.18 × 0.18 mm	0.34 × 0.12 × 0.10 mm	0.16 × 0.04 × 0.04 mm
Crystal shape	prismatic	prismatic	rod
Crystal colour	brown	green-brown	red
θ range for data collection	2.21−25.80°	2.17−25.81°	3.87−39.93°
Temperature	173 K	173 K	297 K
Limiting indices	$-14 \le h \le 14$	$-14 \le h \le 14$	$-9 \le h \le 9$
	$-18 \le k \le 18$	$-19 \le k \le 19$	$-13 \le k \le 13$
	$-20 \le l \le 20$	$-20 \le l \le 20$	$-13 \le l \le 13$
Reflections collected	26619	24164	7211
Independent reflections (R_{int})	5619 (0.0654)	5767 (0.0467)	1811 (0.0721)
Reflections [$I > 2\sigma(I)$]	5325	5472	1695
Data/restraints/parameters	5619/0/343	5767/0/343	1811/0/352
Goodness-of-fit on F^2	1.047	1.034	1.096
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0204	R_1 = 0.0207	R_1 = 0.0218
	wR_2 = 0.0498	wR_2 = 0.0473	wR_2 = 0.0451
R indices (all data)	R_1 = 0.0220	R_1 = 0.0224	R_1 = 0.0254
	wR_2 = 0.0502	wR_2 = 0.0477	wR_2 = 0.0463
Absolute structure parameter	−0.02(2)	−0.03(1)	−0.02(1)
Largest diff. peak/hole	0.411/−0.195 e Å^{-3}	0.831/−0.286 e Å^{-3}	0.197/−0.224 e Å^{-3}
CCDC	178662	178663	178661

X-ray Crystallographic Studies: The data were collected with a STOE-IPDS (Mo-K_α radiation) and an Enraf−Nonius CAD-4 diffractometer (Cu-K_α radiation). Crystal data, data collection, structure refinement and CCDC numbers are given in Table 3. The structures were solved by direct methods (SIR97).[25] Refinement was done by full-matrix least-squares on F^2 (SHELXL-97).[26] CCDC-178662, -178661 and -178663 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].

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