Pyrazole as a Donor Function in Neopentane-Based Tripod Ligands $RCH_2C(CH_2pyrazol\text{-}1\text{-}yl)_{3-n}(CH_2PR_2)_n$ – Synthesis and Coordination Chemistry

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The chlorine functions of $CH_3C(CH_2Cl)_3$, **1**, may be replaced by pyrazolyl (pz) as well as imidazolyl (im) residues under the conditions of nucleophilic substitution leading to tripodal ligands $CH_3C(CH_2X)_3$, X = pz, **2**; X = im, **3**. As a means of introducing two nitrogen donors and one phosphorus donor into a tripod ligand, substitution of the Br and OMs functions in $O(CH_2)_2C(CH_2Br)(CH_2OMs)$, **8**, by nitrogen nucleophiles and subsequent cleavage of the oxetane ring by a phosphide nucleophile to give $HOCH_2C(CH_2PPh_2)(CH_2X)_2$ has been developed, furnishing **10a** (X = pz) and **10d** (X = NEt_2), respectively. For the synthesis of **10a**, K-pz was used as the nucleophile, while **10d** was prepared using azide in the initial step, which then had to be transformed into NEt_2 in two subsequent steps. The nucleophugic functions of the oxetane **8** undergo selective substitution by K-pz and $KPPh_2$ in THF to produce $O(CH_2)_2C(CH_2PPh_2)(CH_2pz)$, **9b**. Phosphide cleavage of the oxetane function leads to $HOCH_2C(CH_2PPh_2)(CH_2PR_2)(CH_2pz)$, R = Ph, **10b**; R = 3,5-$Me_2(C_6H_3)$, **10c**. – The tris(pyrazolyl) tripod ligand **2** reacts with $(MeCN)_3Mo(CO)_3$ to give **2** · $Mo(CO)_3(MeCN)$, **12a**, in which only two of the three donor functions are coordinated. Upon reaction with **10a**, the same reagent gives **10a** · $Mo(CO)_4$, **12b**, with one pyrazolyl coordinated and the other involved in intramolecular hydrogen bonding to the CH_2OH function (N···H–O distance 280 pm). Blocking of the OH function of **10a** by etherification, i.e. to form $EtOCH_2C(CH_2PPh_2)(CH_2pz)_2$, **11**, does not dramatically affect the coordination capabilities with **11** · $Mo(CO)_3(MeCN)$, **12d**, being formed upon treatment with $(MeCN)_3Mo(CO)_3$. Again only one pz function is coordinated to the metal. Bidentate coordination by two phosphorus donors of **10c** is observed in **10c** · $Mo(CO)_3(MeCN)$, **12d**. The dangling arm pz donor function and the CH_2OH group are intermolecularly hydrogen-bonded in this case. When the bulky $P[3,5\text{-}Me_2(C_6H_3)]_2$ substituent of **10c** is replaced by the less sterically demanding PPh_2 donor in **10b**, η^3-coordination is finally observed with the formation of **10b** · $Mo(CO)_3$, **13**. The coordination capabilities of the new ligands are rationalized in terms of the size (six-, seven-, and eight-membered rings) and interference of the chelate cycles. All compounds have been characterized by the usual analytical and spectroscopic methods, with a complete assignment of the NMR data achieved by a combination of 2D-NMR techniques in some cases. The structures of the coordination compounds have additionally been deduced by X-ray methods.

Introduction

The coordination chemistry of tripod ligands has considerable potential in many fields of chemistry: Tripod ligands are essential constituents of many bioinorganic model compounds[1], the stabilization of unconventional ligands by tripod metal templates has found widespread application[2] and catalytic applications of tripod metal templates are a rapidly developing field[3]. As a special type of tripod ligands, molecules containing three different donor groups bonded to a neopentane backbone $CH_3C(CH_2X)(CH_2Y)(CH_2Z)$ have been shown to be productive in coordination chemistry, as well as in catalysis. Sacconi and his group, as well as the group of Bianchini, have made extensive contributions to the application of $CH_3C(CH_2PPh_2)_3$ in preparative and in catalytic chemistry[3][4]. Nevertheless, the potential offered by neopentane-based tripod ligands is still far from being fully exploited. Tripod ligands of this type with up to three different donor groups have only recently become available. While the synthetic strategies for introducing phosphorus donors are well developed[5a][5b][5c][5d][5e], including the EPC synthesis of chiral tripod ligands with three different phosphorus donor groups[5f][5g][5h], general strategies for the synthesis of tripod ligands containing, amongst others, nitrogen donor functions are still lacking. A special route into the chemistry of such ligands based upon the aminolytic cleavage of neopentane-based oxetanes has recently been reported[6] and some particular cases based on the nucleophilic substitution of functionalized neopentane derivatives by azide are known[7].

We report herein on our efforts to devise new methods by which tripod ligands **A** $RCH_2C(CH_2X)(CH_2Y)(CH_2Z)$ with the donor set X, Y, Z containing at least one nitrogen donor can be synthesized.

Special emphasis is put on the introduction of the pyrazolyl donor function, the reason being that this type of functionality has been shown to be highly efficient in tris(pyrazolyl)borate tripod ligands[8]. On the other hand, each

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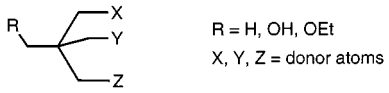


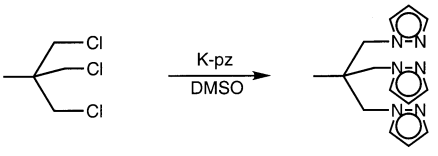
A

pyrazolyl donor function linked to the neopentane backbone in $RCH_2C(CH_2X)(CH_2Y)(CH_2Z)$ increases the ring size in the chelate cage $RCH_2C(CH_2X)(CH_2Y)(CH_2Z)M$ by one over the sterically ideal arrangement of three six-membered rings forming a bicyclooctane-type chelate cage that results when all three donor atoms of X, Y, Z are directly linked to the neopentane carbon skeleton. This increase in ring size (seven-membered chelate rings with one pyrazolyl entity and even eight-membered chelate rings with more than one of these entities) to some extent disfavours the tripodal coordination of such ligands. Given the excellent ligand properties of pyrazolyl ligands on one side and the expected destabilization of η^3-coordination by the introduction of pyrazolyl donor functions into neopentane-based tripod ligands, facile equilibration between η^3- and η^2-coordination modes in such ligand-metal templates may be envisaged. This means that introducing pyrazolyl donor functions into neopentane-based tripod ligands has the potential of allowing the synthesis of coordination compounds in which the pyrazolyl-containing arm of a tripod ligand is easily coordinated and decoordinated, thus reversibly protecting a coordination site at the metal center in the sense of an auxiliary ligand.

This paper deals with the synthesis of tripod ligands $RCH_2C(CH_2X)(CH_2Y)(CH_2Z)$ containing one to three nitrogen donor functions with the other donors being PR_2 groups. The coordination behaviour of these tripod ligands containing up to three pyrazolyl nitrogen donors is probed by characterization of their tricarbonylmolybdenum derivatives.

Synthesis of Tripod Ligands Starting from Tris(chloromethyl)ethane

Tris(chloromethyl)ethane **1**[9] reacts with an excess of potassium pyrazolate (K-pz) in DMSO with substitution of all three chlorine functions by pyrazolyl groups.



1 2

The tripod ligand **2** was obtained by bulb-to-bulb distillation in a kugelrohr apparatus in around 46% yield as a colourless oil, which solidified to give colourless needles after few days. Spectroscopic data and elemental analyses unequivocally confirmed its constitution (Tables 1 and 2, Exp. Section).

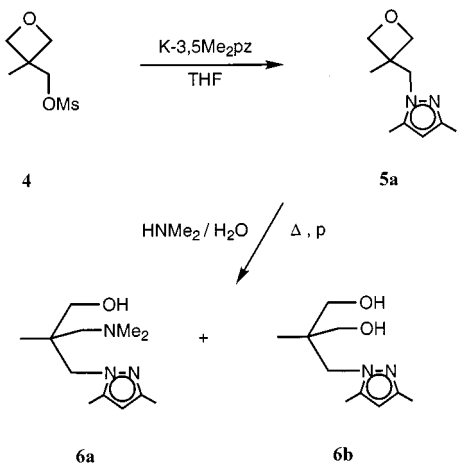
Since the reaction yielding **2** proceeded unexpectedly well – bearing in mind the sluggish reactivity of neopentane derivatives in nucleophilic substitution[7a][10] – it appeared worthwhile to attempt to introduce imidazolyl donors by the same type of straightforward approach. Imidazolyl residues at the neopentane backbone are appealing in so far as it has been shown that multidentate imidazolyl-functionalized ligands may be transformed into multidentate carbene ligands, with the additional merit of making use of the known stability of transition metal-imidazolinylidene carbene bonds[11]. Reaction of the trichloride **1** with potassium imidazolate in DMSO indeed resulted in the tripodal system **3**, albeit in modest yield only.

1 3

Compound **3** was isolated by bulb-to-bulb distillation from the ethereal extract after hydrolysis of the reaction mixture. As a consequence of the high boiling point of free imidazole and of the tripod ligand **3**, appreciable thermal decomposition occurred under the conditions of the distillation. Moreover, increasing the temperature and the reaction time in the synthesis of **3** did not increase the yield because of decomposition of the reaction system into a brown, viscous oil of unknown composition. Compound **3**, as obtained after distillation, consists of colourless needles. Spectroscopic data and elemental analyses confirm the given constitution (Tables 1 and 2, Exp. Section).

Synthesis of Tripod Ligands Starting from Monofunctionalized Oxetanes

Functionalized oxetanes $O(CH_2)_2C(CH_3)(CH_2X)$ have been shown to undergo aminolytic cleavage of the oxetane ring[6][12]. This method works when CH_2OR and CH_2SR substituents are present in the oxetane ring[6]. While this strategy failed in the presence of CH_2PR_2 substituents, we have now found that amino substituents are well tolerated. The pyrazolyl-substituted oxetane **5a** was obtained in good yields from the functionalized oxetane **4** by nucleophilic substitution with potassium 3,5-dimethylpyrazolate (K-3,5-Me_2pz).

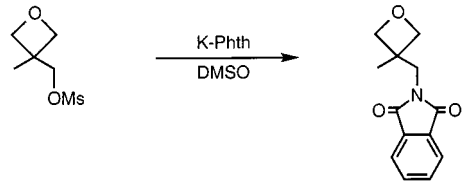


4 5a

6a 6b

Compound **5a** underwent aminolytic cleavage of the oxetane moiety upon treatment with $HNMe_2/H_2O$ at 40 bar/170°C. The product **6a** was accompanied by the bis(hydroxy) compound **6b**. Of course, under the drastic reaction conditions necessary to observe any reaction at all, hydrolytic cleavage effectively competes with aminolytic cleavage. Products **6a/6b** were not completely separable by Vigreux distillation; fractions containing **6a/6b** in ratios up to 4:1 were obtained at best. Compounds **6a/6b** could nevertheless be unequivocally characterized by derivatization (**7a/7b**).

Alternative and potentially more general methods for the exchange of the OMs group by an amine function have been examined. The standard procedure[13] of using potassium phthalimide (K-Phth) as the nitrogen nucleophile works well. While K-Phth is known to react with oxiranes with ring opening[13], the oxetane moiety in **4** stays intact and so this compound can be transformed to the phthalimide derivative **B** in high yields. **B** was fully characterized by its analytical and spectroscopic data (Exp. Section).

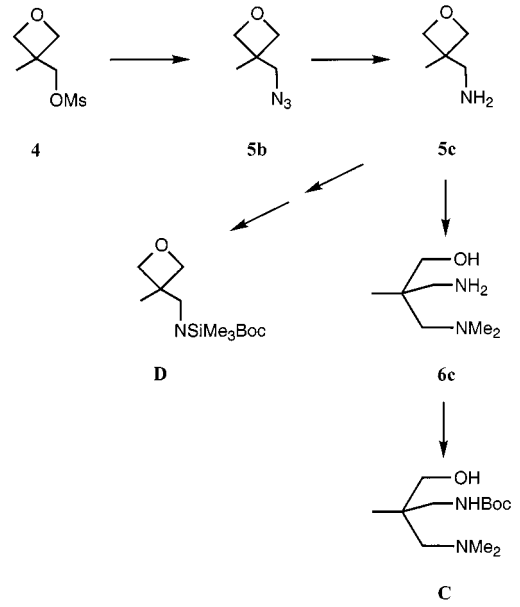


4 **B**

However, any attempt to transform the phthalimide group into an amine function proved problematic. While the cleavage of neopentane-bound phthalimide groups in $CH_3C(CH_2Phth)_3$ has been shown to proceed in the presence of 25% KOH over a period of a few days at room temperature[14], **B** showed no reaction under the same conditions. Hydrazinolysis of **B** was not very effective either; NMR control of the reaction mixture showed that the oxetane functionality was also affected under the drastic conditions necessary (boiling for 10 h). From the reaction mixture obtained after this time, the amine (**5c**) could not be separated.

An alternative strategy starting from **B** might have been possible through its reaction with $LiPPh_2$. If this nucleophile would selectively attack the oxetane ring[5d][5e] of **B**, a subsequent hydrazinolytic cleavage of the phthalimide moiety would no longer be impeded by the reactivity of the oxetane functionality (see above). However, when red $LiPPh_2$ was treated with a solution of colourless **B**, an immediate colour change to deep-green ensued, indicating a reaction at the phthalimide moiety[15]. Reaction control by ^{31}P-NMR spectroscopy showed that a multitude of PPh_2 derivatives of different kinds (^{31}P NMR: δ from −40 to +40) was formed under these conditions. In summary, potassium phthalimide does not appear to be the correct choice of nitrogen nucleophile for the problem at hand.

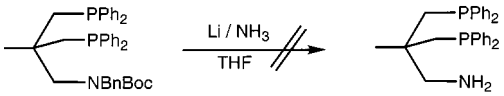
The use of azides as nitrogen nucleophiles is a well-established method, even for polyfunctional and sensitive compounds[16]. This method has previously proved successful in the synthesis of tripod ligands of type **A**[7], and it works as well with **4** as the starting compound. The transformation of **4** into the azide derivative **5b** has been reported in the patent literature, where no details of the procedure were given[17a]. We found that solutions of **4** in DMSO react with a threefold excess of NaN_3 to produce **5b**.



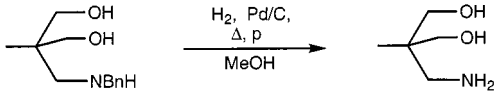
Optimum yields of around 90% were obtained after 30 h at 130°C. Shorter reaction times gave reduced yields (10 h: 50%), while prolonged heating or higher temperatures also reduced the yield (48 h: 55%) (caution: **5b** "AMMO" and several of its polymers are used as explosives[17b] and appropriate care has to be taken in its preparation and work-up). After dilution of the reaction mixture with two equiv. of water, **5b** was extracted into diethyl ether. The presence of **5b** in the ethereal solution was evidenced by an azide band at 2103 cm^{-1} in the IR spectrum. A small amount of the ethereal solution was concentrated to an extent that allowed the characterization of **5b** by ^1H NMR (Exp. Section). The reactivity of **5b** towards PPh_3 gave further proof of its identity: the corresponding iminophosphorane was formed immediately (^{31}P NMR: $\delta = +10.6$), which upon hydrolysis yielded **5c**. Compound **5c** was purified by distillation under reduced pressure, with appropriate care being taken in view of its volatility. The identity of **5c** was obvious from its analytical data (Exp. Section) as well as from its reaction with $HNMe_2/H_2O$ at 30 bar/130°C, which furnished **6c** (Exp. Section). This potential tripod ligand, containing two different nitrogen donors and one oxygen donor, was also fully characterized. Several attempts have been made to further derivatize **6c** with the aim of replacing its OH group by a PPh_2 group. This intended type of transformation requires protection of the NH_2 group. Boc-protection has been found to be adequate, allowing the formation of **C** as a colourless, microcrystalline solid (for analytical and spectroscopic data, see Exp. Section). However, deprotonation of **C** by a minimum of two equivalents of *n*BuLi, subsequent treatment of the product with an excess of MsCl, followed by addition of $LiPPh_2$, resulted in unseparable

product mixtures. These mixtures are not a result of cleavage of the Boc group by *n*BuLi, since **C** can be recovered after treatment with two equivalents of *n*BuLi under the same conditions after hydrolytic work-up. Selective deprotonation of the OH group in the presence of an NHBoc functionality has been reported to occur for HBocNCH(Me)CH_2OH[17c]. In this case, mesylation of the alcohol function was achieved using $MsCl/NEt_3$, whereas in the present case the use of NEt_3 as a base is not feasible since the product obtained after mesylation cannot be purified, presumably due to decomposition by internal cyclization[7a]. If the product mixture is treated with $LiPPh_2$ without any intermediate purification step, a complex mixture of compounds results, with the desired PR_2 substitution occurring only to a minor extent (< 10% according to ^{31}P-NMR data).

A solution to these problems might possibly have been found in replacing the NH function by an $NSiR_3$ function. When **C** was treated with one equivalent of *n*BuLi, and then the reaction mixture was quenched with TMSCl, the *N*-silylated product was obtained. However, mesylation and subsequent reaction with $LiPPh_2$ was again unselective and an unseparable mixture of products was obtained once more. Benzyl-protection of the NHBoc group might appear to be an alternative. However, we found that $CH_3C(CH_2PPh_2)_2(CH_2NBnBoc)$[6], which has been used as a model compound, does not allow for a straightforward debenzylation with the Li/NH_3/THF reagent[18a].



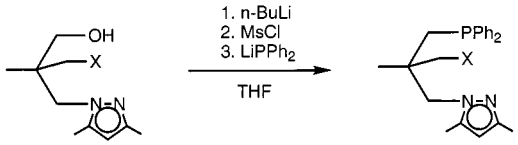
In the present case, only a small yield of $CH_3C(CH_2PPh_2)_2(CH_2NH_2)$ was obtained, which after chromatography was sufficiently pure for identification by NMR spectroscopy with reference to an authentic sample[7b]. Even though the transformation of carbamate-type NBn groups into NH_2 groups by alkali metal in liquid ammonia solutions under carefully controlled conditions is known to work in other cases[18b], the reluctance of the system to undergo a debenzylation reaction does not appear to be due to the presence of the PPh_2 group alone. While hydrogenolytic cleavage of the NBn function is not possible with the model compound due to phosphorus poisoning of the catalyst, it should work well with $CH_3C(CH_2OH)_2(CH_2NBnH)$[6]. With this compound, however, no reaction was observed under conditions using 10% Pd/C catalyst at 1 bar H_2 and 25°C. Only at 60°C under 60 bar H_2 and with reaction times of 12 h was the amine-functionalized product $CH_3C(CH_2OH)_2(CH_2NH_2)$ **E** obtained (Exp. Section).



E

This result suggests that the difficulties observed in the debenzylation reactions are mainly due to the notoriously low reactivity of neopentane derivatives[10]. Even though $CH_3C(CH_2OH)_2(CH_2NH_2)$ is accessible by a debenzylation procedure, its further functionalization is impeded by the same sort of problems as already described for **6c**. The problem of functionalizing **6c** might also potentially be overcome by tracing back the synthesis of **6c** a few steps: Starting from **5c**, Boc-protection and subsequent silylation results in a product **D**, in which the CH_2NH_2 substituent is transformed into a $CH_2NBocSiMe_3$ functionality (see above). When this protected intermediate **D** is treated with $LiPPh_2$, an unseparable reaction mixture nevertheless results (^{31}P NMR: δ from −40 to +40). Tracing one step further back, **5b** produces the iminophosphorano-substituted oxetane $O(CH_2)_2C(CH_3)(CH_2N{=}PPh_3)$ in a clean reaction. If the oxetane moiety of this intermediate would undergo nucleophilic cleavage with $LiPPh_2$, a phosphorus donor might be introduced at such an early stage. However, in practice, this reaction also results in an unseparable mixture (^{31}P NMR) of different phosphorus-containing products.

In contrast to the reluctance of **6c** to undergo further functionalization, **6a** as well as **6b** can be transformed into the phosphorus-containing tripod ligands **7a** and **7b** by the standard procedure[6].



6a : X = NMe_2
6b : X = OH

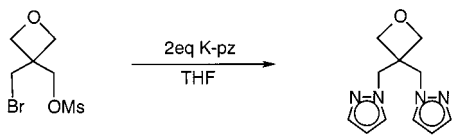
7a : X = NMe_2
7b : X = PPh_2

While **6a** and **6b** are invariably obtained as mixtures (see above), their derivatives **7a** and **7b** can be easily separated by column chromatography owing to the fact that **7a** bearing an NMe_2 group migrates much more slowly than **7b**. Compounds **7** are obtained as colourless, analytically and spectroscopically pure oils (Tables 1 and 2, Exp. Section).

Synthesis of Tripod Ligands Starting from Difunctionalized Oxetanes

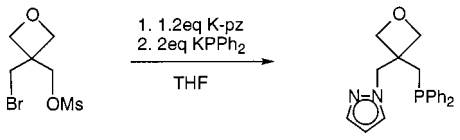
In the synthesis of neopentane-based tripod ligands, the use of difunctionalized oxetanes such as **8**[19] has the additional merit of producing a CH_2OH group at the backbone of the tripod ligand $HOCH_2C(CH_2X)(CH_2Y)(CH_2Z)$, which lends itself to further functionalization of the ligand. Compound **8** has successfully been used as a starting material in the synthesis of phosphorus-containing CH_2OH-functionalized tripod ligands[5d]. Its reaction with nitrogen nucleophiles allows access to mixed donor set tripod ligands containing a CH_2OH group at the quaternary carbon. Thus, **8** reacted with 2 equivalents of K-pz in THF to form the bis(pyrazolyl) derivative **9a**, which was purified by distil-

lation and obtained as a pale-yellow, viscous oil (Exp. Section).



8 **9a**

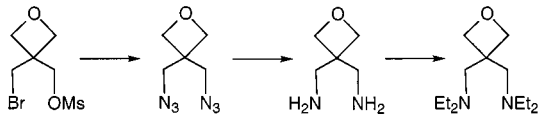
When **8** was treated first with 1.2 equiv. of K-pz and then with 2 equiv. of $KPPh_2$, the substitution product **9b** was obtained in moderate yields. **9b** could be separated from some less polar co-products (including excess $HPPh_2$) by flash chromatography and was obtained as a colourless, microcrystalline solid.



8 **9b**

The identity of the products **9** was established beyond doubt by elemental analyses and mass spectrometry, as well as by NMR spectroscopy (Exp. Section). As usual with 3,3-bis-substituted oxetanes, the symmetric (**9a**) and unsymmetric (**9b**) substitution patterns, respectively, are immediately evident from the multiplicity of the ^{1}H-NMR signals of the oxetane CH_2 groups (Exp. Section)[5d].

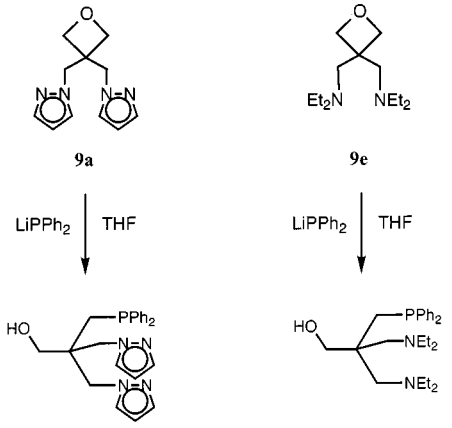
The use of azide as a nucleophile for the substitution of difunctional oxetanes has been reported previously[20a]. Use of **8** as the electrophilically-substituted oxetane instead of $O(CH_2)_2C(CH_2Cl)_2$[20a] was found to increase the yield of **9c** from 25% to around 90%, as inferred from the transformation of **9c** to the corresponding amine **9d** by PPh_3/H_2O.



8 **9c** **9d** **9e**

The NH_2 functions of **9d** could be transformed into NEt_2 functions by treatment with ethyl iodide/K_2CO_3 in ethanol, resulting in a high yield of **9e**[20c]. The oxetane derivatives **9d** and **9e** were fully characterized by their analytical and spectroscopic data (Exp. Section). The potentially explosive **9c** was characterized by its ^{1}H-NMR spectrum, an azide band at 2105 cm^{-1} in the IR spectrum, and its derivatization to **9d**.

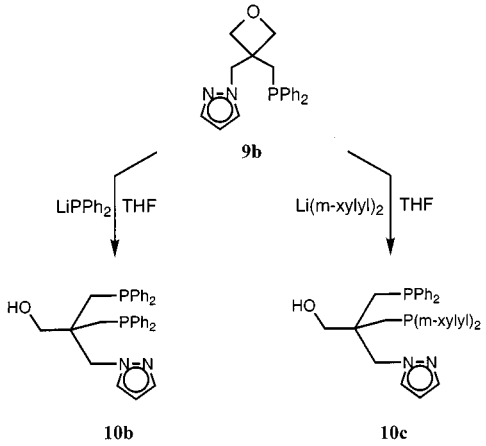
The difunctionalized oxetanes **9a**, **9b**, and **9e** underwent nucleophilic cleavage of the oxetane ring upon treatment with $LiPPh_2$ in boiling THF, resulting in the CH_2OH-functionalized tripod ligands **10**.



9a **9e**

10a **10d**

Compounds **10** were obtained as colourless oils upon chromatographic work-up. Elemental analyses, mass spectra, and NMR data were consistent with the given constitution in each case (Tables 1 and 2, Exp. Section).



9b

10b **10c**

The diastereotopicity of the protons of some of the CH_2 groups in the neopentane framework is of considerable help in assigning the relevant signals to the individual CH_2 entities. For instance, the protons at the pyrazolyl-substituted CH_2 groups of **10a** are diastereotopic, while those of the CH_2PPh_2 and CH_2OH moieties, respectively, are not.

The appearance of the corresponding ^{1}H-NMR signals clearly reflects this difference (Table 1). Analogous arguments help in assigning the ^{1}H-NMR data of the other compounds **10**; the resolution obtainable at 200 MHz does, however, preclude a complete assignment of the ^{1}H-NMR spectra of **10c** and **10d** (Table 1).

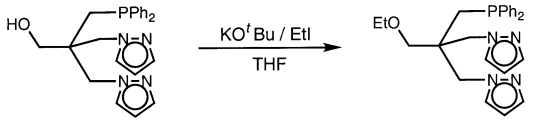
Functionalization of the CH_2OH group at the backbone of tripod ligands is generally hampered by difficulties[21]. Problems arise because of the reduced reactivity of neopentane derivatives as well as due to the fact that tripod ligands, by definition, contain other nucleophilic groups (the ligand entities!) besides the CH_2OH entity. Thus, treatment of **10d** for example with KO*t*Bu/EtI in THF not unexpectedly results in a mixture of products, probably because of partial quaternization of the amine donor functions.

Table 1. Chemical shifts (δ values), integrals [*x*H] and coupling constants *J*[a] in the ^{1}H-NMR spectra of **2**, **3**, **7a**, **7b**, **10a**–**12d**, and **11** (solvent: $CDCl_3$)

	CH_2R	CH_2X	CH_2Y	CH_2Z	*pz-H* [b] *H4*	*H3*	*H5*	*aryl-H*	*other*
2	0.73s [3H] R=H	——4.23s [6H] X=Y=Z=pz——			6.30t [3H]	7.57d [3H]	7.74d [3H]	-	-
3	1.07s [3H] R=H	—3.96s [6H] X=Y=Z=imidazole——			-	-	-	-	6.89s, 7.17s, 7.47s [9H] *imidazole-H*
7a	0.86s [3H] R=H	——2.55m [4H]——— X=PPh_2, Y=NMe_2		3.99s [2H] Z=3,5Me_2-pz	5.76s [1H]	-	-	7.29-7.75m [10H]	2.22-2.48m [12H] pzCH_3, NCH_3
7b	0.93s [3H] R=H	——2.53bs [4H]——— X=Y=PPh_2		4.08s [2H] Z=3,5Me_2-pz	5.79s [1H]	-	-	7.30-7.44m [20H]	2.22s, 2.24s [6H] pzCH_3
10a	3.29s [2H] R=OH	2.15d [2H] *J*=3.6 X=PPh_2	—4.22d, 4.47d [4H]—— *J*=14.3 Y=Z=pz		6.27t [2H]	7.31d [2H]	7.60d [2H]	7.35-7.48m [10H]	-
10b	3.26s [2H] R=OH	——2.47bs [4H]——— X=Y=PPh_2		4.23s [2H] Z=pz	6.18t [1H]	7.09d [1H]	7.49d [1H]	7.30-7.45m [20H]	-
10c	3.25s [2H] R=OH	——2.42m [4H]——— X=PPh_2, Y=P(3,5-Me_2Ph)$_2$		4.25bs [2H] Z=pz	6.20t [1H]	———6.94-7.51[18H]———			2.27bs [12H] xylyl-CH_3
10d	3.25s [2H] R=OH	2.33m [4H] *J*=4.0 X=PPh_2	—2.44-2.78m [12H]—— Y=Z=NEt_2		-	-	-	7.32-7.57m [10H]	1.00t [12H] $^3J_{HH}$=7.2 NCH_2CH_3 6.66bs [1H] O*H*
11	3.11s [2H] R=OEt	2.31bs [2H] X=PPh_2	—4.38d, 4.50d [4H]—— *J*=14.2 Y=Z=pz		6.30t [2H]	———7.35-7.77[14H]———			1.08t [3H] $^3J_{HH}$=6.8, OCH_2CH_3, 3.06q [2H] $^3J_{HH}$=6.8, OCH_2CH_3

[a] $J = {}^2J_{HH}$ unless otherwise stated, coupling constants in Hz. – [b] All pyrazolyl-H′s (except for **7a** and **7b**) give broad signals due to $^3J_{HH}$ coupling (unresolved at 200 Mhz) and integrate as 1 H.

The pyrazolyl residues, being more resistant to electrophilic attack compared to the NEt_2 nucleophiles, should not be prone to problems resulting from quaternization and, indeed, **10a** is transformed to its ethyl ether derivative without complications. The complete set of analytical and spectroscopic data obtained for **11** is in accord with its proposed constitution (Tables 1 and 2, Exp. Section).

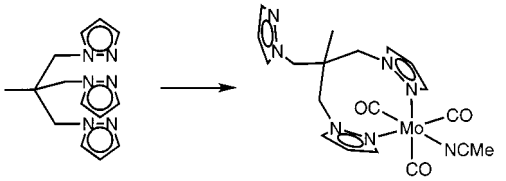


10a **11**

Coordination Chemistry

The coordination behaviour of the novel ligands was tested with $(MeCN)_3Mo(CO)_3$ as the substitution-labile precursor[22]. With the tris(pyrazolyl)-substituted ligand **2**, displacement of only two MeCN groups was observed, resulting in the $Mo(MeCN)(CO)_3$ derivative **12a**, in which **2** acts as a bidentate ligand.

On the basis of its mass spectrum and its ν(CO) IR data, **12a** might appear to be a compound of the composition **2**·$Mo(CO)_3$, containing η^3-coordinated **2** (Table 5, Exp. Section). The ^{1}H-NMR data obtained for **12a**, however, clearly demonstrate that only two pyrazolyl functions are coordinated, while the third one plays the role of a dangling arm (Table 3). The signals attributable to the CH_2pz groups show a clear 2:1 intensity pattern, with the signals of the coordinated residues significantly shifted compared to those of the dangling arm CH_2pz entity (Table 3). This 2:1 pattern is also evident in the ^{13}C-NMR data of **12a** on inspection of the signals of the CH_2pz and pyrazolyl carbons



2 **12a**

(Table 4). The presence of a coordinated acetonitrile can also be deduced by NMR (Tables 3 and 4). Even if the shift imposed on the MeCN ligand by coordination is not always large enough to allow unequivocal differentiation between a coordinated and a non-coordinated acetonitrile, the relative intensity of the MeCN signal in the ^{1}H-NMR spectrum of **12a** shows that just one MeCN is present in each molecule (Table 3), which, in accord with the 18-electron rule and the findings described below (for **12c**, **12d**), leads to the given constitution for **12a**.

Table 2. Chemical shifts (δ values) and coupling constants J[a] in the $^{13}C\{^1H\}$-NMR spectra of **2**, **3**, **7a**, **7b**, **10a−10d**, and **11** (solvent: $CDCl_3$)

	CH_2R	CH_2X	CH_2Y	CH_2Z	*Cq*	pz-*C* [d]			*aryl-C*	*other*
						C4	*C3*	*C5*		
2	19.8 R=H	——56.2, X=Y=Z=pz——			42.8	105.7	140.0	132.2	-	-
3	19.3 R=H	——52.4, X=Y=Z=imidazole——			40.2	-	-	-	-	122.2,128.2 139.5, imidazole
7a	23.1d $^3J_{CP}$= 11.0 R=H	36.9d $^1J_{CP}$=14.7 X=PPh_2	55.6d $^3J_{CP}$=9.2 Y=pz	68.0d $^3J_{CP}$=7.4 Z= NMe_2	42.8d $^2J_{CP}$=12.9	104.9	147.3	140.0	128.7-133.6m	12.3, 14.0 pzCH_3, 49.3 NCH_3
7b	26.0m R=H	—40.6m X=Y=PPh_2——		57.4m Z=pz	41.2	105.1	148.0	140.3	129.2-133.8m	12.4, 13.9 pzCH_3
10a	65.2m R=OH	32.1m X=PPh_2	——54.9m Y=Z=pz——		46.7	105.6	140.0	132.3	128.9-139.8m	-
10b	68.8m R=OH	—35.0m X=Y=PPh_2——		58.4m Z=pz	46.7	105.5	139.8	131.7	128.9-139.3m	-
10c	68.9m R=OH	—34.9m X=Y=PPh_2——		58.4m Z=pz	45.5m	105.6	139.8	131.9	128.8-138.3m	21.8 xylyl-CH_3
10d	69.7 $^3J_{CP}$= 11.0 R=OH	34.3d $^1J_{CP}$=16.4 X=PPh_2	——61.6d $^3J_{CP}$=7.4—— Y=Z=NEt_2		44.7d $^2J_{CP}$=11.0	-	-	-	128.7-140.9m	12.1 NCH_2CH_3, 49.1 NCH_2CH_3
11	71.9 $^3J_{CP}$= 8.1 R=OEt	31.9d $^1J_{CP}$=17.6, X=PPh_2	—54.8m $^3J_{CP}$=9.1—— Y=Z=pz		45.5d $^2J_{CP}$=12.6	105.5	139.7	132.2	128.8-139.5m	15.5 OCH_2CH_3 65.5 OCH_2CH_3

[a] Coupling constants in Hz; all signals are singlets unless otherwise stated.

Table 3. Chemical shifts (δ values), integrals [xH] and coupling constants J[a] in the ^{1}H-NMR spectra of **12a−12d** and **13**

	CH_2R	CH_2X	CH_2Y	CH_2Z	pz-*H* [d]			*aryl-H*	*other*
					H4	*H3*	*H5*		
12a [b]	0.14s [3H] R=H	3.57d, 3.90d [2H] J=14.4 X=pz (c.)	3.90d, 4.31d [2H] J=14.4 Y=pz (c.)	4.13m, 4.40m [2H] Z=pz (n.c.)	6.36 (n.c.) 6.43, 6.51 (c.)	——7.45, 7.63 (n.c)—— ——7.47-8.43m (c.)——		-	0.49s [3H] *Me*CN
12b [c]	——1.39-1.57m, 2.43-2.95m, 3.28-3.43m, 3.64-3.76m, 4.12-4.28m [8H] CH_2P, CH_2N, CH_2O				6.20-6.48m [2H]	——7.36-8.60m [14H]——			-
12c [b]	2.31d, 2.62d [2H] $^3J_{HH}$ = 9.8, R=OEt	1.39d, 2.89d [2H] J=12.8 X=PPh_2	4.28d, 5.37d [2H] J=14.0 Y=pz (c.)	4.10d, 4.28d [2H] J=14.0 Z=pz (n.c.)	6.33 (n.c.) 6.47 (c.)	7.56 (n.c.) 7.84 (c.)	7.42 (n.c.) 8.85 (c.)	8.14m [4H] H_o, 7.32-7.35m [4H] H_m,7.36bs [2H] H_p	1.57s [3H] *Me*CN, 1.05t [3H] $^3J_{HH}$= 6.8 OCH_2CH_3, 2.17q, 2.76q [2H] $^3J_{HH}$ = 6.8 OCH_2CH_3
12d [c]	3.25bs [2H] R=OH	——2.42m [4H]—— X=PPh_2, Y=P(3,5-Me_2Ph)$_2$		4.21bs [2H] Z=pz (n.c.)	6.18 (n.c.)	——6.89-8.28m [18H]——			1.51s [3H] *Me*CN, 2.17-2.65bs [12H] xylyl-CH_3
13 [c]	3.54bs [2H] R=OH	—2.18dd, 2.64dd [4H]— J=14.0 $^2J_{HP}$ = 4.8/ 5.8 X=Y=PPh_2		4.00bs [2H] Z=pz	6.40 (c.)	——7.26-8.26m [22H]——			-

[a] $J = {}^2J_{HH}$ unless otherwise stated, coupling constants in Hz. − [b] Solvent: CD_2Cl_2; the CD_2Cl_2 was condensed into the NMR tubes prior to flame sealing. − [c] Solvent: $CDCl_3$. − [d] c. = coordinated, n. c. = non-coordinated; all pyrazolyl-H′s give broad signals and integrate as 1 H unless otherwise stated.

Table 4. Chemical shifts (δ values) and coupling constants J[a] in the $^{13}C\{^1H\}$-NMR spectra of **12a−12d** and **13**

	CH_2R	CH_2X	CH_2Y	CH_2Z	Cq	pz-C [d]			*aryl-C*	*other*
						C4	*C3*	*C5*		
12a [b]	19.2	54.7	54.8	55.7	43.9	105.9 (n.c.)	140.6 (n.c.)	132.1 (n.c.)	-	3.1
	R=H	X=pz (c.)	Y=pz (c.)	Z=pz (n.c.)		106.9 (c.)	147.1 (c.)	135.2 (c.)		*Me*CN
						107.1 (c.)	147.5 (c.)	135.7 (c.)		
12b[c]	68.4	28.4bs	52.3m	55.7m	45.5bs	105.9 (n.c.)	———	128.5-144.3 (m)	———	-
	R=OH	X=PPh_2	Y=pz (c.)	Z=pz (n.c.)		107.0 (c.)				
12c [b]	68.2	28.4d	51.4d	54.8d	45.1d	105.9 (n.c.)	139.6 (n.c.)	130.6 (n.c.)	128.4m C_m/C_i,	2.6, 121.3
	R=OEt	$^1J_{CP}$=7.4	$^3J_{CP}$=5.5	$^3J_{CP}$=12.9	$^2J_{CP}$=	107.0 (c.)	144.2 (c.)	135.2 (c.)	131.4d $^4J_{CP}$=	*Me*CN,
		X=PPh_2	Y=pz (c.)	Z=pz (n.c.)	3.7				10.1 C_p, 135.7d	15.2, 65.8
									$^2J_{CP}$= 14.7 C_o	OCH_2CH_3

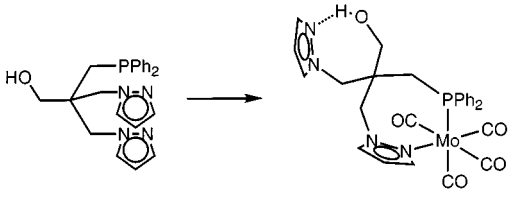
[a] Coupling constants in Hz; all signals are singlets unless otherwise stated. − [b] Solvent: CD_2Cl_2; the CD_2Cl_2 was condensed into the NMR tubes prior to flame sealing. − [c] Solvent: $CDCl_3$. − [d] c. = coordinated, n. c. = non-coordinated.

Table 5. Chemical shifts (δ values) and coupling constants J in the $^{31}P\{^1H\}$-NMR spectra and ν_{CO} IR bands (CH_2Cl_2) of **12a−12d** and **13**

	^{31}P NMR [δ values]	IR {ν_{CO} [cm-1]}
12a[a]	-	1913 (vs), 1783 (s, br).
12b[b]	+ 18.4 (s).	2019 (s), 1903 (vs, br).
12c[a]	+ 18.4 (s).	1923 (vs), 1801 (s, br).
12d[b]	+16.6 (d, 1P, $^2J_{PP}$ = 23.7 Hz), +17.7 (d, 1P, $^2J_{PP}$ = 23.7 Hz).	1925 (vs), 1814 (s, br).
13[b]	+ 21.1 (s).	1936 (vs), 1825 (s, br).

[a] Solvent: CD_2Cl_2; the CD_2Cl_2 was condensed into the NMR tubes prior to flame sealing. − [b] Solvent: $CDCl_3$.

While η^3-coordination did not occur with **2**, having three pyrazolyl donor functions, it appeared probable that the exchange of one pz donor by a PPh_2 group might favour the facial coordination of ligands such as **10a**. While **2** would form a chelate cage with three condensed eight-membered chelate cycles, only one eight-membered cycle and two seven-membered cycles would result from the η^3-coordination of **10a**. However, reaction of **10a** with



10a **12b**

$(MeCN)_3Mo(CO)_3$ affords **12b** as the only isolable product.

The presence of an $Mo(CO)_4$ group in **12b** is evident from the ν(CO) bands, as well as from its mass spectrum (Table 5, Exp. Section). The formation of $Mo(CO)_4$ derivatives from $(MeCN)_3Mo(CO)_3$ is well-documented in tripod coordination chemistry[6][21b]. The ^1H-NMR spectrum of **12b** cannot be completely resolved at 200 MHz; nevertheless, the groups of signals show the expected integral ratios (Table 3). For the bridging hydrogen evident in the solid-state structure (see below), no signal could be assigned, nor could an appropriate band be found in the IR spectrum of **12b**.

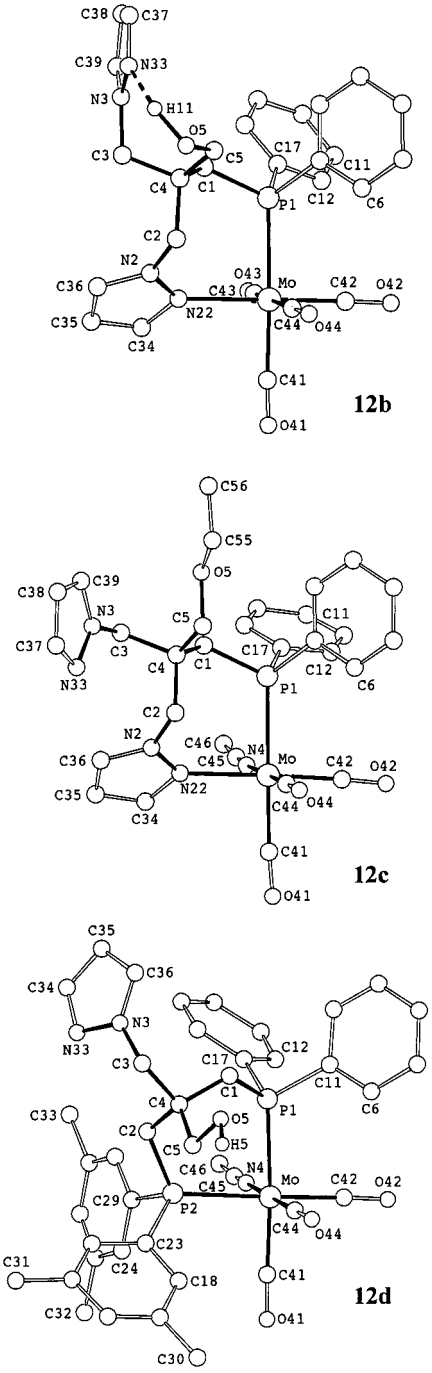
Crystals of **12b** suitable for X-ray analysis were obtained from dichloromethane by vapour-phase diffusion with petroleum ether (40/60). The structure of **12b**, as determined by single-crystal X-ray analysis (Table 8)[23a], is shown in Figure 1: η^2-coordination of the ligand by one pyrazolyl and one phosphorus donor results in the formation of a seven-membered chelate cycle. The tendency of the pyrazolyl ligand to enforce coplanarity between the bonds radiating from the two nitrogen centers in the ring (torsion angle Mo−N−N−C 1.9°, Table 6) results in a characteristic puckering at the other positions of the seven-membered ring, which is also observed for the corresponding entity in **12c** (Figure 1, Table 6).

A peculiar feature of the structure of **12b** is the formation of a strong OH−N hydrogen bond between the dangling arm pyrazolyl entity and the CH_2OH group. The corresponding N−O distance amounts to only 280 pm; the position of the bridging hydrogen has been successfully refined (Table 6).

A seven-membered ring is formed, with the OH group and the pyrazolyl entity linked by the hydrogen bond (Figure 1). With the coplanarity of the H−N−N−C fragment of this ring, its conformation is similar to that observed for the chelate ring (for torsion angles, see Table 6). Since it appears that in **12b** (see also **12d**) the OH proton competes successfully with the metal in coordinating the second pyrazolyl function of **10a**, η^3-coordination of a ligand of the type **10a** might possibly have resulted when the OH function of **10a** was transformed into the OEt function of **11**. However, it was found that **11** produces **12c** when reacted with $(MeCN)_3Mo(CO)_3$, in which again only two donor functions coordinate to the metal center (Figure 1). One pyrazolyl donor and the ethoxy group remain uncoordinated.

The conformation of the seven-membered chelate cycle closely resembles that observed for **12b** (for torsion angles, see Table 6). On the other hand, the rotational orientation

Figure 1. Conformations as observed for **12b**, **12c**, and **12d** in the solid state[a]



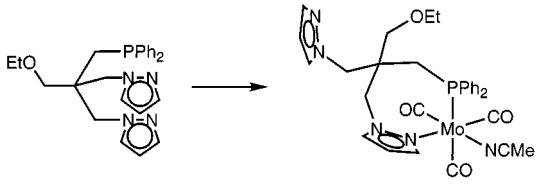
[a] The numbering scheme selected for compounds **12** allows direct comparison with the data given in ref.[6].

of the dangling arm functions is distinctly different from the situation in **12b**, where these donor functions are connected by a strong hydrogen bond (Table 6, Figure 1). Since the conformations of the chelate rings in **12b** and **12c** are nevertheless almost identical, this means that there is little interference between the conformation of the chelate ring at the metal center and the orientation of the substituents at C4 (Figure 1, Table 6). The spectroscopic data obtained

Table 6. Selected bond lengths [pm], bond angles [°], and torsion angles [°] for **12b**, **12c**, and **12d**[a]

	12b	**12c**	**12d**
Mo−P1	251.4 (1)	254.4 (2)	251.7 (1)
Mo−N22 (P2)	230.2 (2)	228.3 (4)	252.7 (1)
Mo−C41	200.6 (3)	197.2 (6)	198.1 (7)
Mo−C42	194.6 (3)	194.0 (5)	195.9 (5)
Mo−C43	204.1 (3)	–	–
Mo−C44	202.5 (3)	193.4 (5)	194.6 (5)
Mo−N4	–	222.0 (4)	220.6 (4)
P1−Mo−N22 (P2)	88.4 (1)	88.0 (1)	84.1 (1)
N33−H11	172 (6)	–	–
N33−H11−O1	143.3 (3)	–	–
Mo−P1−C11−C6	3.9 (2)	6.3 (3)	−22.5 (5)
Mo−P1−C17−C12	−52.3 (2)	−70.8 (5)	64.4 (6)
Mo−P2−C23−C18	–	–	2.3 (4)
Mo−P2−C29−C24	–	–	82.1 (4)
C44−Mo−P1−C1	−89.0 (1)	−92.6 (2)	−53.7 (2)
Mo−P1−C1−C4	61.7 (2)	62.7 (4)	−33.0 (4)
P1−C1−C4−C2	−50.0 (2)	−46.9 (5)	−30.3 (5)
C1−C4−C2−N2 (P2)	−52.3 (3)	−56.6 (5)	73.9 (5)
C4−C2−N2 (P2)−N22 (Mo)	91.6 (2)	93.4 (5)	−44.6 (4)
C2−N2−N22−Mo	1.9 (2)	5.5 (4)	–
(C2−P2−Mo−P1)	–	–	−9.9 (3)
N2−N22−Mo−P1	−51.5 (2)	−52.5 (3)	–
(P2−Mo−P1−C1)	–	–	42.4 (2)
N22−Mo−P1−C1	7.0 (1)	5.5 (2)	–
C4−C3−N3−N33	−82.5	68.4	80.5
C3−N3−N33−H11	15.0	–	–
N3−N33−H11−O1	40.3	–	–
N33−H11−O1−C5	7.9	–	–
H11 (C55)−O1−C5−C4	−75.5	−164.9	−172.4
O1−C5−C4−C3	43.7	−55.1	−62.2
C5−C4−C3−N3	55.3	−45.4	−174.9
C1−C4−C5−O5	162.6	61.0	54.7
C2−C4−C3−N3	170.9	71.3	−58.1

[a] The numbering scheme is such that chemically equivalent atoms have the same numbers in molecules **12b**, **12c** and **12d**.



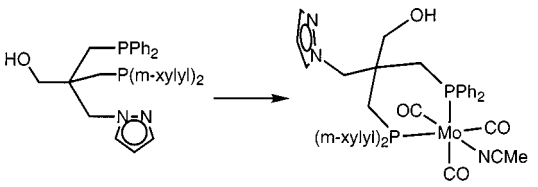
11 **12c**

for **12c** are roughly similar to those obtained for **12a** (Tables 3, 4, and 5). With the structure of **12c** known, this is an indirect proof of the validity of the constitution assigned to **12a**. The ^{1}H-NMR data of **12c** have been analysed in some detail (Table 3). Since at 200 MHz the signals of the five different types of CH_2 groups of **12c** are largely overlapped, a series of 2D-NMR experiments (see Exp. Section) was essential to allow complete assignment of all the individual signals (Tables 3 and 4). A rather astonishing result of these experiments was that the diastereotopic protons of the CH_2P group were found to have their resonances separated by about 1.5 ppm (Table 3). An equally large shift difference was observed for the two diastereotopic protons at the coordinated CH_2pz group (δ = 4.28, 5.37, Table 3). The dangling arm CH_2pz entity has a more normal shift difference (δ = 4.10, 4.28, Table 3) between its diastereotopic protons[6]. The observed strong differentiation between the two

hydrogens at the CH_2 groups in the chelate ring calls for an explanation, since correspondingly large shift differences have, to our knowledge, not hitherto been observed in compounds of neopentane-based ligands, nor in coordination compounds containing the CH_2pz group as part of a ligand[6][24]. It is assumed that the magnetic anisotropy of the dangling arm pyrazolyl entity is responsible for the observed difference in the magnetic shielding of the CH_2 groups within the chelate ring.

The two different types of pyrazolyl entities in **12c** give rise to several ^{1}H resonances in the aromatic region [Table 3; for the numbering scheme, see Figure 4 (Exp. Section)]. The resonance of the central CH group at C4 is well-separated on the highfield side of this range. The resonance of this group is significantly shifted downfield upon coordination (Table 3). An unequivocal assignment of the resonances of the CH groups at C3 and C5 was possible with the combined application of 2D-NMR experiments (Tables 3 and 4, Exp. Section). The ^{1}H signals of the phenyl substituents at the phosphorus could also be fully assigned (Table 3). The ^{13}C-NMR spectrum of **12c** shows an upfield shift for the methylene carbons bound to the coordinated PPh_2 and pyrazolyl entities and a downfield shift for the carbons of the coordinated pyrazolyl entity, while the ^{13}C signals of the non-coordinated CH_2pz group exhibit no shift at all (compared to the free ligand, see Tables 2 and 4). The information gleaned from these NMR experiments is important in so far as no data have hitherto been reported pertaining to the complete and absolute assignment of non-coordinated and coordinated pyrazolyl functions in the same coordination compound[24].

The fact that **11**, containing two pyrazolyl donor functions, acts only as a bidentate ligand, even though the OH group, which competes with the metal coordination of one pyrazolyl donor in the reactions of **10a**, is blocked as an OEt function, indicates that η^3-coordination of neopentane-based tripod ligands will tolerate at most one pyrazolyl donor. An attempt was therefore made to coordinate **10c**, which contains one pyrazolyl and two phosphorus donors, in an η^3-fashion to an $Mo(CO)_3$ fragment. Again, under standard conditions, only bidentate coordination of **10c** was observed, with the $Mo(MeCN)(CO)_3$ fragment coordinated to the two phosphorus donors of the ligand.



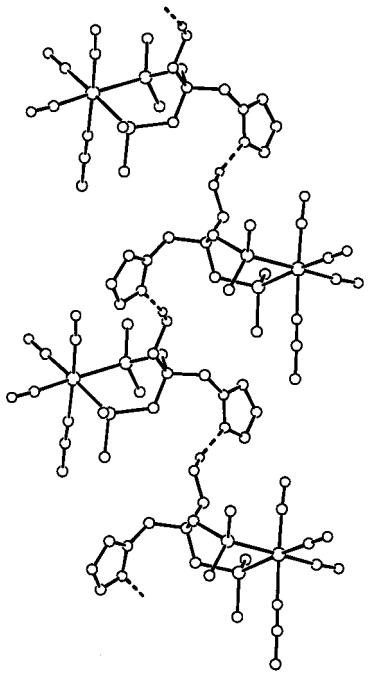
10c **12d**

The presence of a dangling arm pyrazolyl function is indicated by the ^{1}H-NMR data, where the CH_2pz group as well as the CH group at C4 of the pyrazolyl ring show their resonances in the ranges expected for non-coordinated CH_2pz groups (cf. **12c**, Table 5). The coordination of the two phosphorus donors is evident from the ^{31}P-NMR data (Table 3). From the mass spectrum of **12d**, the η^2-coordination of the ligand is not apparent since, as with **12a** and **12c**, the MeCN group is no longer present in the ions detected; [**10c**·$Mo(CO)_3^+$] is the ion with the highest *m*/*z* ratio observed.

The given constitution of **12d** was unequivocally proven by X-ray analysis. Small single crystals of **12d** were obtained by vapour-phase diffusion of petroleum ether (40/60) into the reaction mixture after it had been reduced to half of its original volume. The crystals were found to be very sensitive to air and moisture, but could be subjected to X-ray analysis when immersed in perfluorinated polyether oil and immediately cooled to −70°C (Exp. Section). The coordination of the two phosphorus donors leads to the formation of a six-membered chelate cycle (Figure 1). The conformation of the chelate ring does not correspond to a distinct chair-type arrangement (almost C_s symmetric), which has been observed in quite a number of related structures derived from neopentane-based tripod ligands in an η^2-coordination mode[6][25]. It does not conform to a twistboat arrangement either, which is again found in the structures of some closely related molecules[6][25]. In this context, the structure of $CH_3C(CH_2PPh_2)_2(CH_2Cl)Mo(CO)_4$[23b] is of interest, in which the chelate cycle adopts a distorted chair conformation (P1−C1−C2−P2 = 62.5°, see below). This compound was prepared in order to study the reactivity of the CH_2Cl group with the phosphorus donors protected by an $Mo(CO)_4$ entity − a strategy which has proved useful in certain ligand syntheses[26]. Its structure was analysed in order to get some appraisal of the accessibility of the CH_2Cl group to nucleophiles. The chlorine function has been found to point outwards, away from the molybdenum center[23b]. In contrast, the presence of two sterically demanding functionalities (CH_2pz, CH_2OH) at the central carbon atom in compound **12d** leads to some irregular distortion, which is best described as a chair conformation with some twist, as indicated by the torsion angle P1−C1−C2−P2 of 35.8°. This angle is close to 0° for a chair or boat conformation and around 70° for a pure twist-boat (see above)[6]. This type of distortion of the chelate ring in **12d** has not previously been observed in the coordination chemistry of neopentane-based tripod ligands acting in an η^2-coordination mode. One reason for the distortion observed in **12d** may be the fact that the pyrazolyl substituent and the OH group are both involved in intermolecular hydrogen bonding. The individual molecules are linked by this hydrogen bonding to form chains spiralling around the 2_1 axis, characterizing the symmetry of the crystal in the space group $P2_1/c$. Figure 2 shows a projection illustrating the arrangement in this infinite spiral.

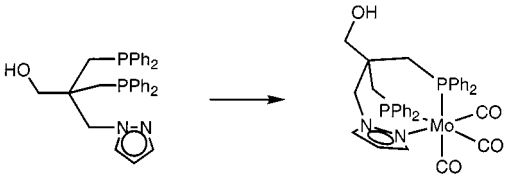
In spite of the unconventional folding of the chelate ring of **12d**, the rotational position of the PPh_2 moieties relative to the idealized octahedral axis of the coordination polyhedron and the rotational position of the phenyl groups relative to the Mo−P axis are not dissimilar from those observed in quite a number of other essentially similar compounds (Table 6)[6].

Figure 2. Hydrogen bonding pattern as observed for **12d** in the crystal[a]



[a] For the sake of clarity, the aryl groups are represented by their *ipso*-carbon atom only; for structural features of **12d** see also Figure 1 and Table 6.

The idea that a tripod ligand of type **A** with only one pyrazolyl donor group and two phosphorus donors should be capable of η^3-coordination appears to be ruled out at first glance by the η^2-coordination observed for **12d**. However, it may be argued that the steric bulk introduced by the 3,5-dimethylphenyl substituents at P2 may be a factor in favouring η^2-coordination, which, as shown for the solid-state structure of **12d**, is then additionally stabilized by intermolecular hydrogen bonding. To verify this argument, the reactivity of **10b** towards $(MeCN)_3Mo(CO)_3$ was tested. While with this ligand intermolecular hydrogen bonding might also favour η^2-coordination, the reduced steric demand of **10b** − two PPh_2 groups instead of one PPh_2 and one $P(3,5\text{-}Me_2Ph)_2$ group − might successfully compete, such that η^3-coordination could result. Such a facial coordination of **10b** is in fact observed, with the $Mo(CO)_3$ derivative **13** being formed.

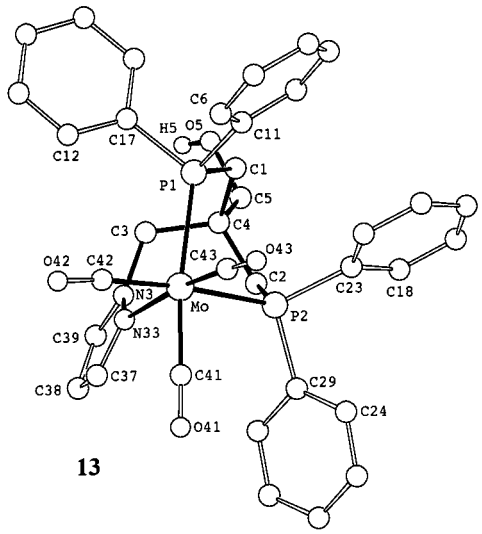


10b **13**

The fact that the ligand **10b** is coordinated in an η^3-binding mode cannot, of course, convincingly be deduced from the appearance of the molecular ion in the mass spectrum (see above), nor is it proved by the observation of the ν_{CO} IR pattern, even though this corresponds to the $A_1 + E$ envelope [Table 5, expected idealized local C_3 symmetry for this type of coordination of the $Mo(CO)_3$ chromophore]. The coordination of the two phosphorus donors on the other hand is clearly evident from the ^{31}P-NMR data (Table 5). The fact that the pyrazolyl donor is coordinated as well is at least not contradicted by the corresponding ^{1}H-NMR data (Table 3). The NMR data give convincing evidence for the fact that the OH group is not coordinated to the metal (Table 3).

Again, the constitution was unambiguously proved by an X-ray analysis performed on well-formed needles obtained from dichloromethane solutions of **13** by vapour-phase diffusion with petroleum ether (40/60). Two crystallographically independent molecules **13** are observed in the crystal (Figure 3). The overall conformations of the two molecules are rather similar, as shown by the torsion angles given in Table 7 (even the torsional positions of the aryl substituents are almost equivalent in the two symmetrically independent species within the crystal).

Figure 3. Conformation as observed for **13/1** in the solid state[a]



13

[a] **13/1** and **13/2** designate the two crystallographically independent molecules in the crystal of **13**. The structure of **13/2** corresponds in its overall arrangement to the structure shown for **13/1**. The numbering scheme chosen for **13** allows for the direct comparison with the data given in ref.[6].

The relative arrangement of the aryl substituents is in accord with a pattern previously described for η^3-coordinated tripod ligands containing two PPh_2 groups and one nitrogen donor[6], even though the chelate cage of **13** contains two seven-membered and only one six-membered cycle, while the cages of comparable molecules[6] contain the standard set of three condensed six-membered cycles. The main difference between the two individual molecules **12** within the crystal is a different orientation of the CH_2OH group relative to the chelate cage (Table 7). This difference in orientation results from the fact that, of the two independent molecules, one is engaged as a proton donor in a hydrogen bond, with one carbonyl group of the other molecule acting as the proton acceptor. The interaction is very weak (d_{O-O} = 299 pm, d_{O-H} = 229 pm, O−H−O =

Table 7. Selected bond lengths [pm], bond angles [°] and torsion angles [°] for **13/1** and **13/2**[a]

	13/1	13/2
Mo1−P1	254.7 (2)	253.9 (2)
Mo1−P2	250.7 (2)	250.9 (2)
Mo1−N3	232.4 (5)	230.3 (5)
Mo1−C41	194.4 (6)	194.1 (6)
Mo1−C42	196.9 (7)	196.6 (6)
Mo1−C43	192.5 (6)	191.7 (7)
P1−Mo1−P2	82.9 (1)	82.8 (1)
P1−Mo1−N3	94.8 (1)	95.1 (1)
P2−Mo1−N3	83.4 (1)	82.4 (1)
Mo1−P1−C1−C4	36.8 (5)	32.9 (5)
Mo1−P2−C2−C4	42.9 (5)	37.5 (5)
Mo1−N3−C3−C4	49.0 (5)	46.4 (5)
P1−C1−C2−P2	−39.7	−33.7
C1−C4−C5−O1	−60.7	55.6
Mo1−P1−C11−C6	−60.1 (5)	−77.1 (5)
Mo1−P1−C17−C12	11.2 (6)	2.3 (6)
Mo1−P2−C23−C18	−169.1 (4)	−159.4 (5)
Mo1−P2−C29−C24	−100.9 (5)	−100.7 (5)
H_z1−P1−C11−C6	−28.9	−45.1
H_z1−P1−C17−C12	−44.6	−52.6
H_z2−P2−C23−C18	142.0	154.6
H_z2−P2−C29−C24	−58.5	−56.7

[a] The numbering scheme adopted for **13/2** relates chemically equivalent atoms by adding 100 to the numbers used in **13/1** (not including molybdenum). The torsion angles given refer to a selection of enantiomers such that the skew of the chelate scaffolding has the same sense for both individual molecules.

144.2°), but is clearly present, as found in the solid-state structure. The OH group of the second molecule shows no close contacts to other hydrogen-accepting positions within the crystal.

The interatomic distances within the five individual molecules (**12b−d** and two molecules **13/1** and **13/2** in the crystal of **13**) are in rather close agreement. The Mo−P bond lengths span a range approximately between 250 and 255 pm (Tables 6 and 7). The Mo−N distances to the pyrazolyl donors are similarly found in a narrow range (228−233 pm), while the coordinated acetonitriles in **12c** and **12d** show significantly shorter Mo−N distances (220−222 pm). The Mo−C(CO) distances are in the usual range. A significant shortening of the Mo−C(CO) bond *trans* to to the pyrazolyl donor is observed in all molecules (Mo−C42 for **12b−d**, Mo−C43 for **13/1**, **13/2**). The Mo−C(CO) bonds *trans* to the acetonitrile ligands are also significantly shorter (Mo−C44 in **12c/d**) than the Mo−C(CO) bonds that are *trans* to an Mo−P bond. This observation reflects the higher donor/acceptor ratio of the nitrogen donors relative to a phosphane ligand. The bite angles P−Mo−N and P−Mo−P, respectively, span a range between 82° and 95° (Tables 6 and 7); angles smaller than 90° are generally observed. An angle of over 90° occurs only in **13**, where in both of the two independent molecules one of the P−Mo−N angles has a value around 95°. This large angle appears to be the result of the steric strain within the seven-membered chelate cycles. This strain leads to a folding of these cycles (Figure 3), which increases the steric burden on one of the phosphorus donors (P1), while relieving the burden on the other (P2). The angle P1−Mo−N33 responds to this strain by increasing accordingly. The presence of strain in the chelate cage of **13** is also indicated by the conformation of the six-membered chelate cycle, which, although in a situation where the chelate cage consists of three condensed six-membered rings, i.e. the normal tripod metal templates $RCH_2C(CH_2X)(CH_2Y)(CH_2Z)M$, is invariably found in an approximate boat arrangement[27]. In **13**, there is an appreciable twist in the boat conformation of this ring (P1−C1−C2−P2 = −39.7°, P101−C101−C102−P102 = −33.7°), which is similar to the twist observed in **12d**, where steric strain was also invoked as an explanation (see above).

Conclusions

1. It is found that pyrazolyl as well as imidazolyl donors may be incorporated into neopentane-based tripod ligands by means of nucleophilic substitution reactions with potassium pyrazolate and potassium imidazolate, respectively.

2. It is shown that the oxetane ring of substituted oxetanes $O(CH_2)_2C(CH_3)(CH_2X)$ undergoes aminolytic cleavage to furnish $CH_3C(CH_2X)(CH_2Y)(CH_2OH)$ systems, with X being an amine or a pyrazolyl substituent and Y being an amine function.

3. It is demonstrated that starting from $O(CH_2)_2$-$C(CH_2Br)(CH_2OMs)$, by selective substitution of the nucleophugic groups and subsequent nucleophilic cleavage of the oxetane moiety, chiral tripod ligands $HOCH_2C(CH_2PR_2)(CH_2Y)(CH_2Z)$ with mixed nitrogen/phosphorus donor sets may be obtained.

4. It is observed that potential tripod ligands $HOCH_2$-$C(CH_2pz)_{3-n}(CH_2PR_2)_n$ tend to act as bidentate chelate ligands when less than two phosphorus donors are present. The size of the chelate ring is invoked as an explanation, with this argument being corroborated by X-ray analysis.

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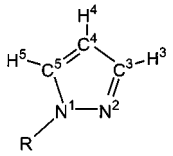
Experimental Section

All manipulations involving phosphanes were carried out under an argon atmosphere by means of standard Schlenk techniques and were monitored by TLC (Macherey-Nagel & Co., Polygram SIL G/UV_{254}). − The aminolytic cleavage of oxetanes was carried out in an HR 100 stainless steel high-pressure laboratory reactor (Berghof/Maasen GmbH) equipped with inlet and outlet valves and a manometer. − The bulb-to-bulb distillations were performed in a kugelrohr apparatus (Büchi). − All solvents were dried by standard methods[28] and distilled under argon. The solvents $CDCl_3$ and CD_2Cl_2 used for the NMR spectroscopic measurements were degassed by three successive "freeze-pump-thaw" cycles and dried over 4 A molecular sieves. − NMR: Bruker Avance DPX 200 at 200.13 MHz (^1H), 50.323 MHz ($^{13}C\{^1H\}$), 81.015 MHz ($^{31}P\{^1H\}$), T = 298 K, chemical shifts (δ) in ppm with respect to $CHCl_3$ (^1H: δ = 7.27, ^{13}C: δ = 77.0) and CH_2Cl_2 (^1H: δ = 5.32, ^{13}C: δ = 53.5)

as internal standards. ^{31}P chemical shifts (δ) in ppm with respect to 85% H_3PO_4 (^{31}P: δ = 0) as external standard. − 2D-NMR experiments: DQF-COSY[29a], TOCSY[29b], NOESY[29c], HMQC[29d], and HMBC[29e] experiments were performed in order to allow the complete assignment of protons and carbons in **12c**. − IR: Bruker FT-IR IFS-66, CaF_2 cells. − MS (EI): Finnigan MAT 8320; fast-atom bombardment (FAB) xenon, matrix: 4-nitrobenzyl alcohol. − Melting points: Gallenkamp MFB-595 010; uncorrected values. − Elemental analyses: Microanalytical Laboratory of the Organisch-Chemisches Institut, Universität Heidelberg. The procedures used for determining the carbon content often give falsely low values when Mo is present in a compound owing to the formation of incombustible Mo carbide; nitrogen values generally tend to be to low as well. − The silica gel (Kieselgel z.A. 0.06−0.2 mm, J. T. Baker Chemicals B.V.) used for chromatography was degassed at 1 mbar for 24 h and saturated with argon. A solution of 2.5 M *n*BuLi in hexanes was used for deprotonations. $Mo(CO)_6$ was sublimed before use. **1**[9], $(MeCN)_3Mo(CO)_3$[22], **4**[19] and **8**[5d] were prepared according to literature procedures. All other chemicals were obtained from commercial suppliers and used without further purification.

Figure 4. NMR numbering scheme for the pyrazolyl ring[24]



X-ray Structure Determinations: Suitable crystals were taken directly out of the mother liquor, immersed in perfluorinated polyether oil and fixed to a glass capillary at 200 K. The measurements for **12d** and **13** were carried out on a Siemens P4 four-circle diffractometer (equipped with a low temperature device) with graphite-monochromated Mo-K_α radiation. The measurements for **12b** and **12c** were carried out on a Siemens CCD/SMART System (equipped with a low temperature device) also with graphite-monochromated Mo-K_α radiation. All calculations were performed using the SHELXT-PLUS[30] software package. Structures were solved by direct methods with the SHELXS-86 program[30a] and refined with the SHELX-93 program[30b]. Graphical handling of the structural data during solution and refinement was performed with XPMA[31]. An absorption correction (ψ-scan, Δψ = 10°) was applied to the data for **12d** and **13**. An empirical absorption correction was applied in the cases of **12b** and **12c**. Atomic coordinates and anisotropic parameters of the non-hydrogen atoms were refined by full-matrix least-squares calculations. Data for the structure determination are compiled in Table 8.

Ligand Synthesis

1,1,1-Tris(pyrazol-1-yl-methyl)ethane (**2**): 3.40 g (50 mmol) of pyrazole was dissolved in 100 ml of DMSO and deprotonated at 0°C with 5.61 g (50 mmol) of KO*t*Bu. After warming to room temperature, 1.58 g (9 mmol) of tris(chloromethyl)ethane **1** in 10 ml of DMSO was added. The resulting mixture was stirred for 12 h at 120°C. The solution was then cooled and the DMSO was evaporated in vacuo (10^{-1} mbar). 60 ml of water was added to the oily brown residue and after stirring for 20 min., the brown solution was extracted with 50 ml portions of diethyl ether (5×). The combined organic phases were concentrated in vacuo (10^{-1} mbar). The brown residue was divided into three portions, which were separately purified by bulb-to-bulb distillation. After removing the pyrazole at 120°C (0.5 mbar), the temperature was raised further and 1.11 g (4.1 mmol, 46%) of **2** was obtained as colourless needles (200−250°C/0.5 mbar). − MS (EI); *m/z* (%): 270 (10) [M^+], 189 (100) [$M^+ - CH_2pz$], 121 (59) [$M^+ - CH_2pz - pz$], 81 (45) [CH_2pz^+]. − $C_{14}H_{18}N_6$ (270.34): calcd. C 62.19, H 6.71, N 31.10; found C 61.86, H 6.88, N 29.90.

1,1,1-Tris(imidazol-1-yl-methyl)ethane (**3**): 4.08 g (60 mmol) of imidazole was dissolved in 120 ml of DMSO and deprotonated at 0°C with 6.73 g (60 mmol) of KO*t*Bu. After warming to room temperature, 1.76 g (10 mmol) of tris(chloromethyl)ethane **1** in 10 ml of DMSO was added. The resulting mixture was stirred for 14 h at 120°C. The solution was then cooled and the DMSO was evaporated in vacuo (10^{-1} mbar). 70 ml of water was added to the reddish-brown residue. After stirring for 20 min, the brown solution was extracted with 30 ml portions of THF (5×) and subsequently with 20 ml portions of dichloromethane (3×). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated in vacuo (10^{-1} mbar). The resulting orange-coloured oil was divided into three portions, which were separately purified by bulb-to-bulb distillation. 0.35 g (1.3 mmol, 13%) of **3** as colourless crystals (230°C/0.02 mbar) was obtained. − MS (EI); *m/z* (%): 271 (67) [M^+], 189 (28) [$M^+ - CH_2$imidazole], 121 (100) [$M^+ - CH_2$imidazole − imidazole], 81 (81) [CH_2imidazole$^+$]. − $C_{14}H_{18}N_6$ (270.34): calcd. C 62.19, H 6.71, N 31.10; found C 61.75, H 6.57, N 30.67.

3-Methyl-3-(3,5-dimethylpyrazol-1-yl-methyl)oxetane (**5a**); 4.80 g (60 mmol) of 3,5-dimethylpyrazole was dissolved in 150 ml of THF and deprotonated at 0°C with 6.74 g (60 mmol) of KO*t*Bu. The solution was then allowed to warm to room temperature. In a second flask, 9.00 g (50 mmol) of 3-methyl-3-(methylsulfonyloxymethyl)oxetane **4** in 100 ml of THF was cooled to 0°C. The potassium pyrazolate solution was then added and the reaction mixture was refluxed for 4 h. The jelly-like mixture was then quenched by the addition of 50 ml of water and the aqueous phase was extracted with 30 ml portions of diethyl ether (2×). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and distilled through a 20 cm Vigreux column at 1 mbar. 6.85 g (38 mmol, 76%) of **9a** was obtained as a colourless oil (b.p. 128−133°C, 1 mbar). − ^1H NMR ($CDCl_3$): δ = 1.18 (s, 3 H, CqCH_3), 2.13, 2.15 (2s, 6 H, pzCH_3), 4.05 (s, 2 H, CH_2pz), 4.29, 4.70 (2d, 4 H, oxetane-CH_2, $^2J_{HH}$ = 5.8 Hz), 5.72 [s, 1 H, C*H(4)*pz]. − ^{13}C NMR ($CDCl_3$): δ = 11.8, 13.9 (2s, pzCH_3), 22.3 (s, CqCH_3), 41.5 (s, Cq), 54.5 (s, CH_2pz), 81.0 (s, oxetane-CH_2), 105.2 [s, *C(4)*pz], 139.5 [s, *C(5)*pz], 148.0 [s, *C(3)*pz]. − MS (EI); *m/z* (%): 180 (30) [M^+], 149 (55) [M^+ − CHO], 109 (100) [CH_2pz^+], 96 (22) [pz^+]. − $C_{10}H_{16}N_2O \cdot 1/3\ H_2O$* (180.25): calcd. C 64.49, H 9.02, N 15.04; found C 64.47, H 9.05, N 15.05. *The water content was inferred from the analytical results, which were well reproducible.

3-Azidomethyl-3-methyloxetane (**5b**): 18.0 g (0.1 mol) of 3-methyl-3-(methylsulfonyloxymethyl)oxetane **4** and 19.0 g (0.3 mol) of NaN_3 were dissolved in 300 ml of DMSO. This mixture was stirred vigorously for 30 h at 120°C. After cooling to room temperature, 600 ml water was added and the solution was carefully extracted with 100 ml portions of diethyl ether (4×). The combined organic phases were concentrated in vacuo (10^{-1} mbar) to half of the initial volume (CAUTION: explosive). A sample of 1 ml was concentrated to dryness at 10^{-2} mbar (0°C) in order to obtain spectroscopic data of **5b**. − IR (Et_2O): ν = 2103 (s, $-N_3$). − ^1H NMR ($CDCl_3$): δ = 1.28 (s, 3 H, CH_3), 3.48 (s, 2 H, CH_2N), 4.31, 4.39 (2d, 4 H, $^2J_{HH}$ = 6.0 Hz, oxetane-CH_2). − ^{13}C NMR ($CDCl_3$): δ = 23.1 (s, *C*H_3), 40.5 (s, *Cq*), 58.1 (s, *C*H_2N), 79.6 (s, oxetane-*C*H_2).

3-Aminomethyl-3-methyloxetane (**5c**): 23.7 g (90 mmol) of PPh_3 was added slowly to a well-stirred ethereal solution of **5b**. Evolution

Table 8. Crystal data for **12b**, **12c**, **12d**, and **13**

Compound	**12b**	**12c**	**12d**	**13**
Formula	$C_{27}H_{25}N_4O_5PMo$	$C_{30}H_{32}N_5O_4PMo$	$C_{41}H_{43}N_3O_4P_2Mo \cdot 0.5\ CH_2Cl_2 \cdot 1.5$ MeOH	$C_{35}H_{32}N_2O_4P_2Mo \cdot 2\ CH_2Cl_2$
molecular mass [g]	612.43	653.53	799.71	702.54
crystal size [mm]	0.3 × 0.3 × 0.3	0.3 × 0.3 × 0.2	0.05 × 0.05 × 0.2	0.3 × 0.3 × 0.2
crystal system	triclinic	monoclinic	monoclinic	triclinic
space group (No.)[30c]	*P*1 (2)	$P2_1/n$ (14)	$P2_1/c$ (14)	*P*1 (2)
a [pm]	936.62(2)	908.9(5)	1612.76(2)	1021.2(2)
b [pm]	1065.85(1)	2005.2(3)	1183.87(1)	1649.3(4)
c [pm]	1479.42(2)	1634.8(4)	2470.21(1)	2078.4(7)
α [°]	72.90(1)	90	90	93.02(2)
β [°]	72.12(1)	92.38(4)	93.71(1)	92.63(2)
γ [°]	72.94(1)	90	90	90.70(2)
V [10^6 pm^3]	1309.6(1)	2976.9(2)	4706.5(1)	3491.7(2)
Z	2	4	4	4
d_x [g cm^{-3}]	1.553	1.447	1.242	1.494
μ [mm^{-1}]	0.61	0.54	0.45	0.66
transition (min)	0.80	0.81	0.90	0.78
transition (max)	0.92	0.87	0.99	0.90
T [K]	200	200	200	200
no. rflns. for cell param. refinm.	all	25	all	26
scan range	6.4° ≤ 2Θ ≤ 54.6°	4.8° ≤ 2Θ ≤ 51.0°	3.3° ≤ 2Θ ≤ 51.8°	3.9° ≤ 2Θ ≤ 48.1°
scan speed [° min^{-1}]	–	ω = 6	–	ω = 12
no. rflns. measured	6881	5964	20889	11468
no. unique rflns.	5039	5531	7791	10683
no. rflns. observed	4730	4005	6519	7306
observation criterion	$I \geq 2\sigma$	$I \geq 2\sigma$	$I \geq 2\sigma$	$I \geq 2\sigma$
no. param. refined	443	462	514	868
resid. el. density [10^{-6} e pm^{-3}]	0.57	0.59	1.39[a]	0.71
R_1/R_w [%] (refinement on F^2)	3.1/10.4	5.5/11.3	6.1/23.6[a]	5.3/11.8

[a] Due to badly resolved, disordered solvent molecules.

of nitrogen was observed over a period of two hours. The reaction mixture was then stirred at room temperature for 10 h [reaction control: ^{31}P NMR: PPh_3, δ = −7.2, imidophosphorane (R−N=PPh_3), δ = +10.6; IR: ν = 2103 (s, R−N_3)]. Subsequently, addition of 1.8 ml of water and refluxing for two hours led to cleavage of the imidophosphorane (reaction control: ^{31}P NMR: O=PPh_3, δ = +28.2). The solvent was removed under reduced pressure (100 mbar) using a trap (−70°C). The residue was distilled through a 10 cm Vigreux column at 20 mbar while the head was cooled to −10°C (using a cryostat) and the collecting flask was ice-cooled. 9.1 g (82 mmol, 82%) **5c** was obtained as a colourless oil; b.p. of 40°C (20 mbar). − ^{1}H NMR ($CDCl_3$): δ = 1.21 (s, 3 H, CH_3), 2.86 (s, 2 H, CH_2N), 4.35, 4.41 (2d, 4 H, $^2J_{HH}$ = 5.8 Hz, oxetane-CH_2). − ^{13}C NMR ($CDCl_3$): δ = 21.1 (s, *C*H_3), 40.4 (s, *Cq*), 49.1 (s, *C*H_2S), 80.2 (s, oxetane-*C*H_2). − MS (EI), *m/z* (%): 129 (9) [$M^+ \cdot H_2O$], 101 (10) [M^+]. − $C_5H_{11}NO \cdot 1/10$ DMSO/H_2O* (110.76): calcd. C 56.39, H 10.74, N 12.65; found C 56.29, H 10.97, N 12.91. *The DMSO content was estimated by NMR; the water content was inferred from elemental analysis.

3-(tert-Butyloxycarbonyl)aminomethyl-3-methyloxetane (*Boc-***5c**): Boc-protection of **5c** was carried out on a 25 mmol sample according to a previously published procedure[6]. After work-up, Boc-**5c** was obtained as a colourless oil, which could be crystallized by overlayering a dichloromethane solution with petroleum ether (40/60). After two days, 4.07 g (20 mmol, 81%) of Boc-**5c** was isolated in the form of colourless needles. − ^{1}H NMR ($CDCl_3$): δ = 1.26 (s, 3 H, CqCH_3), 1.42 (s, 9 H, *Boc*), 3.26 (d, 2 H, $^3J_{HH}$ = 6.4 Hz, CH_2N), 4.31, 4.43 (2d, 4 H, $^2J_{HH}$ = 5.8 Hz, oxetane-CH_2), 5.25 (bs, 1 H, N*H*). − ^{13}C NMR ($CDCl_3$): δ = 22.3 (s, CqCH_3), 28.7, 79.7, 158.1 (3s, *Boc*), 40.5 (s, *Cq*), 47.4 (s, *C*H_2N), 80.5 (s, oxetane-*C*H_2). − MS (EI), *m/z* (%): 201 (2) [M^+], 145 (69) [$M^+ - C_4H_9$], 115 (100) [NBoc$^+$]. − $C_{10}H_{19}NO_3$ (201.27): calcd. C 59.68, H 9.52, N 6.96; found C 59.63, H 9.57, N 6.89.

3-(tert-Butyloxycarbonyl)(trimethylsilyl)aminomethyl-3-methyloxetane (**D**): Deprotonation of Boc-**5c** with 1 equiv. of *n*BuLi in THF at −70°C followed by addition of 1.2 equiv. TMSCl yielded **D** after removal of the solvent in vacuo (10^{-1} mbar). − ^{1}H NMR ($CDCl_3$): δ = 0.28 (s, 9 H, Si*Me*$_3$), 1.37 (s, 3 H, CqCH_3), 1.51 (s, 9 H, *Boc*), 3.18 (s, 2 H, CH_2N), 4.18, 4.68 (2d, 4 H, $^2J_{HH}$ = 5.8 Hz, oxetane-CH_2).

3-Phthalimidomethyl-3-methyloxetane (**B**): 9.0 g (50 mmol) of 3-methyl-3-(methylsulfonyloxymethyl)oxetane **4** and 10.2 g (55 mmol) of potassium phthalimide were dissolved in 400 ml of DMSO. This mixture was stirred vigorously for 4 h at 120°C. After cooling to 50°C, the DMSO was removed in vacuo (10^{-1} mbar) and 50 ml of water was added to the residue. The product was extracted with 40 ml portions of dichloromethane (4×). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and concentrated at 10^{-1} mbar. The resulting light-yellow oil crystallized after 2 h at 0°C. 10.3 g (44.6 mmol, 89%) of **B** was obtained as colourless needles after washing the crystalline material with portions of petroleum ether (40/60) (3 × 20 ml). − ^{1}H NMR ($CDCl_3$): δ = 1.29 (s, 3 H, CqCH_3), 3.80 (s, 2 H, CH_2N), 4.27, 4.64 (2d, 4 H, $^2J_{HH}$ = 6.2 Hz, oxetane-CH_2), 7.66−7.81 (m, 4 H, *aromat. H*). − ^{13}C NMR ($CDCl_3$): δ = 22.6 (s, Cq*C*H$_3$), 41.1 (s, *Cq*), 44.7 (s, *C*H$_2$N), 80.9 (s, oxetane-*C*H$_2$), 123.6−134.5 (*aromat. C*). − MS (EI), *m/z* (%): 231 (67) [M^+], 201 (100) [$M^+ - CH_2O$]. − $C_{13}H_{13}NO_3$ (231.25): calcd. C 67.52, H 5.67, N 6.06; found C 67.25, H 5.66, N 6.05.

The aminolytic cleavage of the oxetanes **5a** and **5c** was performed in an autoclave (see above) according to a previously published procedure[6].

(±)-2-Dimethylaminomethyl-2-(3,5-dimethylpyrazol-1-yl-methyl)-2-methylpropan-1-ol (**6a**) *and 2-Methyl-2-(3,5-dimethylpyrazol-1-yl-methyl)propane-1,3-diol* (**6b**): 9.0 g (50 mmol) of **5a** was heated in an aqueous dimethylamine solution. After one week at 40 bar and 170°C, a product mixture of **6a/6b** in an overall yield of around 40% was obtained. The products **6a/6b** could not be completely separated by distillation through a 20 cm Vigreux column (10^{-1} mbar). Two fractions were collected above 100°C (**I**: 3.05 g, 130−150°C, **6a/6b** ratio = 4:1 and **II**: 1.81 g, 150−165°C, **6a**7**6b** ratio = 1:5; ratios estimated from ^{1}H-NMR data).

(±)-2-Aminomethyl-2-dimethylaminomethyl-2-methylpropan-1-ol (**6c**): 2.22 g (20 mmol) of **5c** was heated in an aqueous dimethylamine solution. The reaction was complete after 48 h at 30 bar and 140°C. After work-up, distillation through a micro Vigreux column in vacuo yielded 1.31 g (9 mmol, 45%) of **6c** as a colourless oil, b.p. 56°C (1.4 mbar). − ^{1}H NMR ($CDCl_3$): δ = 0.77 (s, 3 H, CqCH_3), 2.27 (s, 6 H, NMe_2), 2.37 (m, 2 H, CH_2N), 2.57, 2.80 (2bd, 2 H, $^2J_{HH}$ = 12.6 Hz, CH_2N), 2.95 (bs, 2 H, NH_2), 3.53 (bs, 2 H, CH_2O). − ^{13}C NMR ($CDCl_3$): δ = 20.0 (s, CqCH_3), 40.0 (s, *Cq*), 48.3, 67.2 (s, *C*H$_2$N), 48.8 (s, NMe_2), 71.1 (s, *C*H$_2$O). − $C_7H_{18}N_2O\cdot 1/4\ H_2O$ (146.23): calcd. C 55.78, H 12.37, N 18.58; found C 55.67, H 11.68, N 18.25.

(±)-2-(tert-Butyloxycarbonyl)aminomethyl-2-dimethylaminomethyl-2-methylpropan-1-ol (*Boc*-**6c**): Boc-protection of **6c** was carried out on a 6.4 mmol sample according to a previously published procedure[6]. After work-up, Boc-**6c** was obtained as a colourless oil, which solidified after a few days at 0°C yielding 1.56 g (6.3 mmol, 99%) of Boc-**6c** as colourless crystals. − ^{1}H NMR ($CDCl_3$): δ = 0.83 (s, 3 H, CqCH_3), 1.48 (s, 9 H, *Boc*), 2.29 (m, 2 H, CH_2N), 2.34 (s, 6 H, NMe_2), 2.93 (bs, 1 H, N*H*), 3.16, 3.45 (2m, 4 H, CH_2N, CH_2OH), 5.01 (bs, 1 H, O*H*). − ^{13}C NMR ($CDCl_3$): δ = 20.0 (s, Cq*C*H$_3$), 28.8, 79.8, 158.5 (3s, *Boc*), 40.7 (s, *Cq*), 45.6, 67.6, 68.9 (3s, *C*H$_2$N, *C*H$_2$O), 49.0 (s, NMe_2). − MS (EI), *m/z* (%): 246 [M$^+$], 173 [M$^+$ − C_4H_9O]. − $C_{12}H_{26}N_2O_3$ (246.35): calcd. C 58.51, H 10.64, N 11.37; found C 58.25, H 10.51, N 11.07.

2-Aminomethyl-2-methylpropane-1,3-diol (**E**): 3.95 g (19 mmol) of 2-benzylaminomethyl-2-methylpropane-1,3-diol[6] was dissolved in 50 ml of methanol. 0.6 g of 10% Pd/C was added and the mixture was stirred under 60 bar H_2 pressure at 60°C for 12 h (the reaction was monitored by ^{1}H NMR). The catalyst was then removed by filtration and the residue was distilled through a micro Vigreux column. 1.65 g (13.9 mmol, 73%) of **E** was obtained as a colourless oil (b.p. 63−65°C, 23 mbar). − ^{1}H NMR ($CDCl_3$): δ = 0.76 (s, 3 H, CqCH_3), 2.80 (s, 2 H, CH_2N), 3.58 (bs, 4 H, CH_2OH). − ^{13}C NMR ($CDCl_3$): δ = 18.3 (s, Cq*C*H$_3$), 40.1 (s, *Cq*), 48.2 (s, *C*H$_2$N), 68.8 (s, *C*H$_2$OH). − MS (EI), *m/z* (%): 120 [M$^+$]. − $C_5H_{13}NO_2$ (119.16): calcd. C 50.40, H 11.60, N 11.75; found C 49.59, H 10.41, N 10.75.

2-(tert-Butyloxycarbonyl)aminomethyl-2-methylpropane-1,3-diol (*Boc*-**E**): Boc-protection of **E** was carried out on a 10 mmol sample according to a previously published procedure[6]. After work-up, 2.1 g (9.6 mmol, 96%) of Boc-**E** was obtained as a colourless, microcrystalline solid. − ^{1}H NMR ($CDCl_3$): δ = 0.76 (s, 3 H, CqCH_3), 1.48 (s, 9 H, *Boc*), 3.24 (d, 2 H, $^3J_{HH}$ = 7.0 Hz, CH_2N), 3.42, 3.55 (2d, 4 H, $^2J_{HH}$ = 11.4 Hz, CH_2OH), 3.83 (bs, 1 H, N*H*). − ^{13}C NMR ($CDCl_3$): δ = 17.9 (s, Cq*C*H$_3$), 28.7, 80.7, 158.5 (3s, *Boc*), 41.4 (s, *Cq*), 43.8 (s, *C*H$_2$N), 68.5 (s, *C*H$_2$OH). − MS (EI), *m/z* (%): 220 (13) [M$^+$], 56 (100) [$C_4H_8^+$]. − $C_{10}H_{21}NO_4$ (219.28): calcd. C 54.77, H 9.65, N 6.39; found C 54.73, H 9.69, N 6.22.

Preparation of **7a** and **7b**: The transformation of alcohol functions into PPh_2 groups was performed according to a previously published procedure[6].

2-(Dimethylaminomethyl)-2-(diphenylphosphanylmethyl)-2-(3,5-dimethylpyrazol-1-ylmethyl)ethane (**7a**): Activation of **6a**[6] (fraction **I**, see above) and subsequent substitution with $LiPPh_2$ gave, after flash chromatography, 1.58 g (4 mmol, 33%) of a very viscous oil. − R_f = 0.2 (PE/Et_2O, 2:1). − ^{31}P NMR ($CDCl_3$): δ = −27.0 (s). − MS (EI); *m/z* (%): 393 (14) [M$^+$], 335 (34) [M$^+$ − CH_2NMe_2], 239 (14) [M$^+$ − CH_2NMe_2 − 3,5-Me_2pz], 183 (30) [PPh_2^+], 98 (39) [3,5-Me_2pz$^+$], 58 (100) [$CH_2NMe_2^+$]. − $C_{24}H_{32}N_3P$ (393.51): calcd. C 73.25, H 8.20, N 10.68, P 7.87; found C 72.05, H 8.30, N 10.14, P 7.55.

2,2-Bis(diphenylphosphanylmethyl)-2-(3,5-dimethylpyrazol-1-ylmethyl)ethane (**7b**): Activation of **6b**[6] (fraction **II**, see above) and subsequent substitution with $LiPPh_2$ gave, after flash chromatography, 1.71g (3.2 mmol, 40%) of **7b** as a viscous oil. − R_f = 0.6 (PE/Et_2O, 2:1). − ^{31}P NMR ($CDCl_3$): δ = −27.3 (s). − MS (EI); *m/z* (%): 534 (20) [M$^+$], 457 (100) [M$^+$ − Ph], 349 (5) [M$^+$ − CH_2PPh_2], 199 (8) [$CH_2PPh_2^+$], 185 (13) [PPh_2^+], 78 (4) [Ph$^+$]. − $C_{34}H_{36}N_2P_2$ (534.62): calcd. C 76.39, H 6.79, N 5.24, P 11.59; found C 75.79, H 7.00, N 5.01, P 11.42.

3,3-Bis(pyrazol-1-ylmethyl)oxetane (**9a**): 7.49 g (110 mmol) of pyrazole was dissolved in 300 ml of THF and deprotonated at 0°C with 12.35 g (110 mmol) of KO*t*Bu. After warming to room temperature and stirring for 20 min., a white precipitate of potassium pyrazolate was formed. This suspension was added at 0°C to a solution of 12.96 g (50 mmol) of **8** in 200 ml of THF and the reaction was completed by refluxing for 4 h. The jelly-like mixture was then quenched by the addition of 100 ml of water and the aqueous phase was extracted with 50 ml portions of diethyl ether (2×). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered, and distilled through a 20 cm Vigreux column. 8.90 g (41 mmol, 82%) of **9a** was obtained as a pale-yellow oil (b.p. 138−145°C, 10^{-1} mbar). − ^{1}H NMR ($CDCl_3$): δ = 4.31 (s, 4 H, oxetane-CH_2), 4.68 (s, 4 H, CH_2pz), 6.23 [t, 2 H, $^3J_{HH}$ = 2 Hz, CH(4)pz], 7.37 [d, 2 H, $^3J_{HH}$ = 2 Hz, CH(3)pz], 7.52 [d, 2 H, $^3J_{HH}$ = 2 Hz, CH(5)pz]. − ^{13}C NMR ($CDCl_3$): δ = 45.4 (s, Cq), 54.3 (s, CH_2pz), 78.0 (s, oxetane-CH_2), 105.6 [s, C(4)pz], 131.4 [s, C(5)pz], 140.5 [s, C(3)pz]. − MS (EI); *m/z* (%): 218 (18) [M$^+$], 188 (99) [M$^+$ − OCH_2], 137 (57) [M$^+$ − CH_2pz], 120 (100) [M$^+$ − OCH_2 − pz], 81 (96) [CH_2pz^+], 69 (42) [pzH$^+$]. − $C_{11}H_{14}N_4O$ (218.26): calcd. C 60.53, H 6.47, N 25.67; found C 58.98, H 6.46, N 24.98.

3-(Diphenylphosphanylmethyl)-3-(pyrazol-1-ylmethyl)oxetane (**9b**): 1.63 g (24 mmol) of pyrazole was dissolved in 100 ml of THF and deprotonated at 0°C with 2.69 g (24 mmol) of KO*t*Bu. After warming to room temperature, a white precipitate of potassium pyrazolate was formed. This suspension was added at 0°C to a solution of 12.96 g (50 mmol) of **8** in 200 ml of THF and the reaction was completed by refluxing for 5 h. In another flask, 7.44 g (40 mmol) of $HPPh_2$ was dissolved in 50 ml of THF and deprotonated with 4.49 g (40 mmol) of KO*t*Bu at 0°C. After warming to room temperature and stirring for 20 min., the red potassium phosphide solution was added dropwise to the first reaction mixture, which was maintained at 0°C. After warming to room temperature and stirring for 10 h (the phosphide substitution was monitored by TLC), the then yellow solution was quenched by the addition of 100 ml of deoxygenated water. The aqueous phase was extracted with 50-ml portions of diethyl ether (2×). The combined organic phases were washed with deoxygenated brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting viscous

oil was purified by column chromatography on silica gel using petroleum ether (40/60)/diethyl ether (1:1) as eluent to obtain 3.32 g (10 mmol, 49%) of **9b** as a colourless, microcrystalline powder. – R_f = 0.1 – ^{1}H NMR ($CDCl_3$): δ = 2.43 (bs, 2 H, CH_2P), 4.50 (2d, 4 H, CH_2O, $^2J_{HH}$ = 6.4 Hz), 4.65 (s, 2 H, CH_2N), 6.23 [t, 1 H, $^3J_{HH}$ = 2 Hz, C*H(4)*pz], 7.31 [d, 1 H, $^3J_{HH}$ = 2 Hz, C*H(3)*pz], 7.35–7.49 (10 H, *aromat. H*), 7.55 [d, 1 H, $^3J_{HH}$ = 2 Hz, C*H(5)*pz]. – ^{13}C NMR ($CDCl_3$): δ = 34.7 (d, *C*H_2P), 44.1 (d, *Cq*), 56.9 (s, CH_2N), 80.3 (d, CH_2O), 105.6 [s, *C(4)*pz], 129.0–140.3 (*aromat. C*), 131.1 [s, *C(5)*pz], 140.3 [s, *C(3)*pz]. – ^{31}P NMR ($CDCl_3$): δ = –26.8 (s). – MS (EI); *m/z* (%): 336 (29) [M^+], 305 (48) [M^+ – OCH_2], 199 (40) [$CH_2PPh_2^+$], 183 (100) [M^+ – PPh_2], 121 (73) [M^+ –OCH_2 –CH_2PPh_2], 81 (26) [CH_2pz^+]. – $C_{20}H_{21}N_2OP$ (336.37): calcd. C 71.41, H 6.29, N 8.33, P 9.21; found C 71.34, H 6.48, N 8.32, P 9.16.

3,3-Bis(azidomethyl)oxetane (**9c**)[20a]: Compound **9c** was prepared as described for compound **5b** (see above). Starting with 12.9 g (50 mmol) of **8**, two equiv. of NaN_3 were employed. After careful work-up (CAUTION: explosive), a sample of 1 ml was concentrated to dryness at 10^{-2} mbar (0°C) in order to obtain spectroscopic data of **9c**. – IR (Et_2O): ν = 2105 (s, –N_3). – ^{1}H NMR ($CDCl_3$): δ = 3.48 (s, 4 H, CH_2N), 4.35 (s, 4 H, oxetane-CH_2).

3,3-Bis(aminomethyl)oxetane (**9d**)[20b]: Compound **9d** was prepared as described for compound **5c** (see above). Two equiv. of PPh_3 and of water were employed. 3.9 g (31 mmol, 62%) of **9d** was obtained upon distillation as a colourless oil (b.p. 86°C, 3 mbar), which was found to contain 1/2 equivalent of water (as inferred from the elemental analysis, see also[20b]). – ^{1}H NMR ($CDCl_3$): δ = 1.10 (bs, 4 H, NH_2), 2.97 (s, 4 H, CH_2N), 4.37 (s, 4 H, oxetane-CH_2). – ^{13}C NMR ($CDCl_3$): δ = 43.9 (s, *C*H_2N), 44.6 (s, *Cq*), 78.3 (s, oxetane-*C*). – MS (EI); *m/z* (%): 117 (100) [M^+]. – $C_5H_{12}N_2O \cdot 1/2\ H_2O$ (125.17): calcd. C 47.98, H 10.47, N 22.38; found C 47.49, H 9.92, N 21.39.

3,3-Bis(diethylaminomethyl)oxetane (**9e**)[20c]: 2.32 g (20 mmol) of **9d** and 6.09 g (44 mmol) of K_2CO_3 were dissolved in 40 ml of EtOH. 11.5 ml (144 mmol) of EtI was slowly added, the reaction mixture was refluxed for 12 h, and then concentrated in vacuo to half of its initial volume. To the concentrate, 10 ml of aqueous NaOH (10%) was added and the mixture was extracted with 20 ml portions of dichloromethane (3×). The combined organic phases were washed with deoxygenated brine (2×), dried over $MgSO_4$, filtered, and concentrated in vacuo. Distillation through a 20 cm Vigreux column at 3 mbar furnished 3.01 g (13.2 mmol, 73%) of **9e** as a colourless oil (b.p. 91°C, 3 mbar). – ^{1}H NMR ($CDCl_3$): δ = 1.02 (t, 12 H, $^3J_{HH}$ = 7.2 Hz, NCH_2CH_3), 2.53 (q, 8 H, $^3J_{HH}$ = 7.2 Hz, NCH_2CH_3), 2.74 (s, 4 H, CH_2N), 4.45 (s, 4 H, oxetane-CH_2). – ^{13}C NMR ($CDCl_3$): δ = 11.8 (s, NCH_2CH_3), 44.8 (s, *Cq*), 47.8 (s, NCH_2CH_3), 57.7 (s, *C*H_2N), 80.0 (s, oxetane-*C*). – MS (EI); *m/z* (%): 228 (4) [M^+], 155 (39) [M^+ – NEt_2], 126 (63) [M^+ – NEt_2 – Et], 86 (100) [$CH_2NEt_2^+$]. – $C_{13}H_{28}N_2O$ (228.38): C 68.37, H 12.36, N 12.27; found C 67.70, H 11.71, N 12.14.

Preparation of **10a**–**10d**: 1 equiv. of the appropriately substituted oxetane was dissolved in THF (3 ml per mmol oxetane). In a second flask, 1.2 equiv. of $HPPh_2$ was dissolved in THF (2 ml per mmol $HPPh_2$) and deprotonated at 0°C with 1.2 equiv. of *n*BuLi. After warming to room temperature and stirring for 20 min., the red lithium phosphide solution was added dropwise to the oxetane solution at 0°C. The mixture was allowed to warm to room temperature, while the reaction progress was monitored by TLC. Upon completion (4–10 h), the reaction was quenched by the addition of deoxygenated water. The aqueous phase was extracted with small portions of diethyl ether (3×). The combined organic phases were washed with deoxygenated brine, dried over $MgSO_4$, filtered, and concentrated in vacuo yielding the crude products as colourless oils.

3-(Diphenylphosphanyl)-2,2-bis(pyrazol-1-ylmethyl)propan-1-ol (**10a**): The crude product was purified by column chromatography on silica gel using petroleum ether (40/60)/diethyl ether (1:1) and pure diethyl ether (after elution of $HPPh_2$) to obtain 5.57 g (13.8 mmol, 81%) of **10a** as a colourless, microcrystalline powder. – R_f = 0.15 (Et_2O) – ^{31}P NMR ($CDCl_3$): δ = –29.0 (s). – MS (EI); *m/z* (%): 403 (96) [M^+], 323 (68) [M^+ – CH_2pz], 255 (91) [M^+ – CH_2pz – pz], 199 (82) [$CH_2PPh_2^+$], 121 (100) [$CHPPh^+$], 81 (38) [CH_2pz^+]. – $C_{23}H_{25}N_4OP$ (404.45): calcd. C 68.30, H 6.23, N 13.85, P 7.66; found C 68.31, H 6.40, N 13.17, P 7.53.

2,2-Bis(diphenylphosphanylmethyl)-3-(pyrazol-1-yl)propan-1-ol (**10b**): The crude product was purified by column chromatography on silica gel using petroleum ether (40/60)/diethyl ether (3:2) and pure diethyl ether (after elution of $HPPh_2$) to obtain 2.78 g (5.3 mmol, 78%) of **10b** as a colourless, microcrystalline powder. – R_f = 0.3 (Et_2O) – ^{31}P NMR ($CDCl_3$): δ = –29.5 (s). – MS (EI); *m/z* (%): 522 (12) [M^+], 445 (100) [M^+ – Ph], 367 (55) [M^+ – 2 Ph], 183 (39) [PPh_2^+]. – $C_{32}H_{34}N_2OP_2$ (524.58): C 73.25, H 6.54, N 5.34, P 11.82; found C 73.37, H 6.24, N 5.31, P 11.78.

2-(Diphenylphosphanylmethyl)-2-(3,5-dimethylphenyl)-phosphanylmethyl]-3-(pyrazol-1-yl)propan-1-ol (**10c**): The crude product was purified by column chromatography on silica gel using petroleum ether (40/60)/diethyl ether (3:2) and pure diethyl ether (after elution of the diarylphosphanes) to obtain 1.75 g (3.0 mmol, 82%) of **10c** as a colourless, microcrystalline powder. – R_f = 0.25 (Et_2O) – m.p. 54.9°C. – ^{31}P NMR ($CDCl_3$): δ = –29.5 (d, $^4J_{PP}$ = 8.7 Hz), –29.8 (bs). – MS (EI); *m/z* (%): 577 (20) [M^+], 500 (55) [M^+ – Ph], 472 (35) [M^+ – (3,5-Me_2Ph)], 423 (43) [M^+ – 2 Ph], 241 (19) [P(3,5-Me_2Ph)$_2^+$], 101 (100) [(3,5-Me_2Ph)$^+$]. – $C_{36}H_{40}N_2OP_2$ (578.67): calcd. C 74.71, H 6.97, N 4.84, P 10.71; found C 74.57, H 7.19, N 4.67, P 10.47.

2,2-Bis(diethylaminomethyl)-3-(diphenylphosphanyl)propan-1-ol (**10d**): The crude product was purified by column chromatography on silica gel using petroleum ether (40/60)/diethyl ether (1:1) to obtain 2.23 g (5.4 mmol, 82%) of **10d** as a colourless, viscous oil. – R_f = 0.25. – ^{31}P NMR ($CDCl_3$): δ = –28.4 (s). – MS (EI); *m/z* (%): 413 (3) [M^+], 328 (10) [M^+ – CH_2NEt_2], 183 (12) [$CH_2PPh_2^+$], 86 (100) [$CH_2NEt_2^+$]. – $C_{25}H_{39}N_2OP$ (414.57): calcd. C 72.43, H 9.48, N 6.76, P 7.47; found C 72.34, H 9.56, N 6.65, P 7.48.

3-(Diphenylphosphanyl)-2,2-bis(pyrazol-1-yl-methyl)propyl Ethyl Ether (**11**): 855 mg (2.1 mmol) of **10a** was dissolved in 40 ml of THF and the solution was cooled to 0°C. Addition of 1.18 g (10.6 mmol) of KO*t*Bu yielded a clear, yellow solution. After 20 min., 0.84 ml (10.6 mmol) of EtI in 10 ml of THF was added dropwise. The reaction mixture was stirred overnight at room temperature [TLC control (PE/Et_2O, 3:2): **10a**: R_f = 0.1; **11**: R_f = 0.3]. The reaction was then quenched by the addition of 10 ml of deoxygenated water and the aqueous phase was extracted with 10 ml portions of diethyl ether (2×). The combined organic phases were washed with deoxygenated brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting viscous oil was purified by column chromatography on silica gel using petroleum ether (40/60)/diethyl ether (3:2) to obtain 832 mg (1.9 mmol, 91%) of **11** as a colourless, viscous oil, which solidified after two days. – R_f = 0.3. – ^{31}P NMR ($CDCl_3$): δ = –29.0 (s). – MS (EI); *m/z* (%): 403 (96) [M^+], 323 (68) [M^+ – CH_2pz], 255 (91) [M^+ – CH_2pz – pz], 199 (82) [$CH_2PPh_2^+$], 121 (100) [$CHPPh^+$], 81 (38) [CH_2pz^+]. –

$C_{25}H_{29}N_4OP$ (432.51): calcd. C 69.43, H 6.76, N 12.95, P 7.16; found C 69.39, H 6.81, N 12.99, P 7.16.

Coordination Chemistry

Preparation of **12a**−**12d**, **13**: A stirred solution of 1 mmol ligand in 100 ml of dichloromethane was cooled to −70°C and 0.95 mmol (288 mg) of freshly prepared $(MeCN)_3Mo(CO)_3$ was added. After 2−4 h, all of the $(MeCN)_3Mo(CO)_3$ had dissolved, resulting in a clear, yellow solution. The solvent was then removed at 10^{-1} mbar without heating of the solution. The complexes were recrystallized at 0°C by vapour diffusion of petroleum ether (40−60) into a solution of the crude product in dichloromethane.

η^2-[1,1,1-Tris(pyrazol-1-yl-methyl)ethane]monoacetonitriletricarbonylmolybdenum(0) (**12a**): Yield 398 mg (0.81 mmol, 81%) of **12a** as a brown solid, m.p. 135−138°C (dec). − MS (FAB), *m/z* (%) [Frag.] : 452 (92) [$M^+ - CH_3CN$], 428 (43) [$M^+ - CH_3CN -$ CO], 396 (41) [$M^+ - CH_3CN - 2$ CO], 368 (100) [$M^+ - CH_3CN - 3$ CO]. − $C_{19}H_{21}MoN_7O_3$ (491.36): calcd. C 46.41, H 4.31, N 19.95; found C 44.20, H 4.18, N 18.30.

η^2-P,N-[3-(Diphenylphosphanyl)-2,2-bis(pyrazol-1-ylmethyl)propan-1-ol]tetracarbonylmolybdenum(0) (**12b**): Yield 514 mg (0.8 mmol, 84%) of **12b** as a light-brown solid. Recrystallization afforded 220 mg (0.36 mmol, 36%) of **12b** in the form of yellow crystals suitable for X-ray structural analysis, m.p. 200−205°C (dec). − MS (FAB), *m/z* (%): 614 (4) [M^+], 586 (13) [$M^+ -$ CO], 558 (7) [$M^+ - 2$ CO], 530 (16) [$M^+ - 3$ CO], 502 (21) [$M^+ - 4$ CO], 421 (100) [(**10a**-O)$^+$], 403 (41) [(**10a**)$^+$]. − $C_{27}H_{25}MoN_4O_5P$ (612.43): calcd. C 52.95, H 4.11, N 9.15, P 5.06; found C 51.55, H 3.88, N 8.91, P 5.00.

η^2-P,N-[3-(Diphenylphosphanyl)-2,2-bis-(pyrazol-1-yl-methyl)propyl Ethyl Ether]-monoacetonitriletricarbonylmolybdenum(0) (**12c**): Yield 516 mg (0.79 mmol, 79%) of **12c** as a light-yellow solid. Recrystallization afforded 131 mg (0.20 mmol, 20%) of **12c** in the form of colourless crystals suitable for X-ray structural analysis, m.p. 85°C (dec). − MS (FAB), *m/z* (%): 614 (41) [$M^+ - CH_3CN$], 586 (24) [$M^+ - CH_3CN -$ CO], 558 (39) [$M^+ - CH_3CN - 2$ CO], 530 (77) [$M^+ - CH_3CN - 3$ CO], 449 (100) [(**11**-O)$^+$], 433 (84) [(**11**)$^+$]. − $C_{30}H_{32}MoN_5O_4P$ (653.53): calcd. C 55.14, H 4.94, N 10.72, P 4.74; found C 54.84, H 4.67, N 10.40, P 4.60.

η^2-P,P-{2-(Diphenylphosphanylmethyl)-2-(3,5-dimethylphenyl)phosphanylmethyl]-3-(pyrazol-1-yl)propan-1-ol}monoacetonitriletricarbonylmolybdenum(0) (**12d**): The preparation of **12d** was carried out similarly to that of **12c** above. After 4 h, all of the $(MeCN)_3Mo(CO)_3$ had dissolved, resulting in a clear brown solution, which was concentrated to half of the initial volume and layered with petroleum ether (40−60). After one day at 0°C, small colourless needles suitable for X-ray structural analysis were obtained. The crystals were found to be very sensitive and turned black within seconds on exposure to air. − Yield 152 mg (0.19 mmol, 19%) of **12d**. − MS (FAB), *m/z* (%): 760 (16) [$M^+ - CH_3CN$], 732 (21) [$M^+ - CH_3CN -$ CO], 704 (16) [$M^+ - CH_3CN - 2$ CO], 676 (100) [$M^+ - CH_3CN - 3$ CO], 578 (26) [(**10c**)$^+$]. − $C_{41}H_{43}MoN_3O_4P_2$ (799.71): calcd. C 61.58, H 5.42, N 5.25, P 7.75; found C 61.79, H 6.15, N 4.63, P 7.83.

η^3-[2,2-Bis(diphenylphosphanylmethyl)-2-(pyrazol-1-ylmethyl)propan-1-ol]tricarbonylmolybdenum(0) (**13**): Yield 632 mg (0.9 mmol, 90%) of **13** as a light-yellow solid. Recrystallization afforded 197 mg (0.35 mmol, 35%) of **13** in the form of pale-yellow crystals suitable for X-ray structural analysis, m.p. 190−195°C (dec). − MS (FAB), *m/z* (%): 703 (48) [M^+], 674 (100) [$M^+ -$ CO], 648 (8) [$M^+ - 2$ CO], 619 (32) [$M^+ - 3$ CO]. − $C_{35}H_{32}MoN_2O_4P_2$ (702.54): calcd. C 59.84, H 4.59, N 3.99, P 8.82; found C 59.63, H 5.13, N 3.81, P 8.75.

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