Preparation, Properties, and Reactions of Metal-Containing Heterocycles, XCII[◇]

Steric and Solvent Effects of the Different Reaction Patterns of Activated Alkynes with Diphosphamanganacyclopropanes☆

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The product pattern of the reaction of the alkynes ZC≡CZ (**4**−**11**) [Z = CO_2R: R = Me (**4**), Et (**5**), *n*Pr (**6**), *i*Pr (**7**), *n*Bu (**8**), *n*Pent (**9**), *neo*-Pent (**10**), *cyc*-Hex (**11**)] with the diphosphamanganacyclopropanes $(OC)_4\overline{Mn-P^1P_2^1-P^2}R^2$ (**1**−**3**) depends on the polarity of the employed solvent. Whereas in *n*-hexane the diphosphamanganabicyclo[3.3.0]octadienones **12a**−**q**, the diphosphamanganacyclopentenes **13a**−**h**, and the triphosphamanganabicyclo[3.2.0]heptenones **14a**−**h** are formed, in THF only the five-membered heterocycles **13** occur. Compound **14d** is easily oxidized to the corresponding oxide **15d**. According to X-ray structural analyses, both **14d** and **15d** crystallize in the space group $P\bar{1}$. The Lewis basic properties of the phosphorus atom P^2 in the heterocycle **1** were corroborated by reaction of **1** with $THFCr(CO)_5$ leading to the adduct $(OC)_4\overline{Mn-P^1R_2^1-P^2}(R^2)Cr(CO)_5$ (**16**). Quantitative $^{31}P\{^1H\}$-NMR investigations in $CDCl_3$ enable the determination of the product ratio **13**/**12** as a function of the steric encumbrance of the ester substituents. An increase of the steric hindrance leads to the preferential formation of the monocyclic compounds **13**. If the steric demand at the phosphorus atom P^2 is released, only the bicyclic compounds **12i**−**q** are formed.

Complexes of the late[1−4] and to some extent also of the early[5−12] transition metals play an important role in the cyclotrimerization of alkynes and in the cyclocotrimerization of alkynes with nitriles[13] and phosphaalkynes[14]. With the exception of phosphaalkynes these reactions proceed via metallacyclopropanes and metallacyclopentadienes as intermediates. Depending on the kind of the alkyne, the products are metallacycloheptatrienes or metallabicycloheptadienes[15−18]. Reductive elimination results in the formation of highly substituted benzene and pyridine derivatives, respectively. It is surprising that analogous cyclocotrimerizations with electron-poor alkynes are possible by introduction of the >P=S group which stems from deprotonated diorganylphosphane sulfides[19]. Its alkyne-like character is traced back to similar covalence radii and electronegativities of phosphorus and sulfur. Interestingly, thiaphosphametallacyclopentadienes and thiaphosphametallabicycloheptadienes occur in the same way as intermediates. Thus, a comparable reaction path is adopted as in the above-mentioned cyclotrimerization of alkynes. Oxidative and hydrolytic degradation of thiaphosphamanganabicycloheptadienes lead to regiospecifically substituted thiophenes[20] and furanes[21], respectively.

Between sulfur and the PR fragment exists an isolobal relation[22]. Therefore, comparable reactions should be expected between the corresponding three-membered heterocycles $(OC)_4\overline{Mn-P^1R_2^1-P^2}R^2$[23] and activated acetylenes. Remarkably, a completely different reaction pathway takes place and the formation of diphosphamanganabicyclo[3.3.0]octadienones[24] and diphosphamanganabicyclo[3.1.0]hexenones[24] was observed. Additionally, in one case a diphosphamanganacyclopentene was formed[25]. This different reaction pattern requires further investigations to get an insight into the course of these reactions. This paper focuses on the behavior of activated alkynes toward diphosphamanganacyclopropanes by varying the steric demand of the substituents at the alkynes. An important factor is also the polarity of the employed solvent.

Results and Discussion

1) Behavior of Diphosphamanagancyclopropanes Toward Differently Substituted Alkynes

If the three-membered heterocycles **1**−**3**[23] were treated with an excess of the activated alkynes **4**−**11** in *n*-hexane at ambient temperature, the color of the solutions turned from yellow to deep red within a few minutes. Only in the case of the heterocycle **1** with the steric encumbering *tert*-butyl substituent at the phosphorus atom P^2, three reaction products were obtained which were identified as the diphosphamanganabicyclo[3.3.0]octadienones **12a**, **b**[24], **c**−**h**, the diphosphamanganacyclopentenes **13a**−**h**[25], and the triphosphamanganabicyclo[3.2.0]heptenones **14a**−**h** (Scheme 1). Compounds **12c**−**h** and **13c**−**h** could be separated from **14c**−**h** by employing medium-pressure liquid chromatography (MPLC). Whereas **12c**−**h**, **13d**, and **14d** were isolated and characterized carefully by different analytical methods, the completely analogous mono- and bicyclic heterocycles

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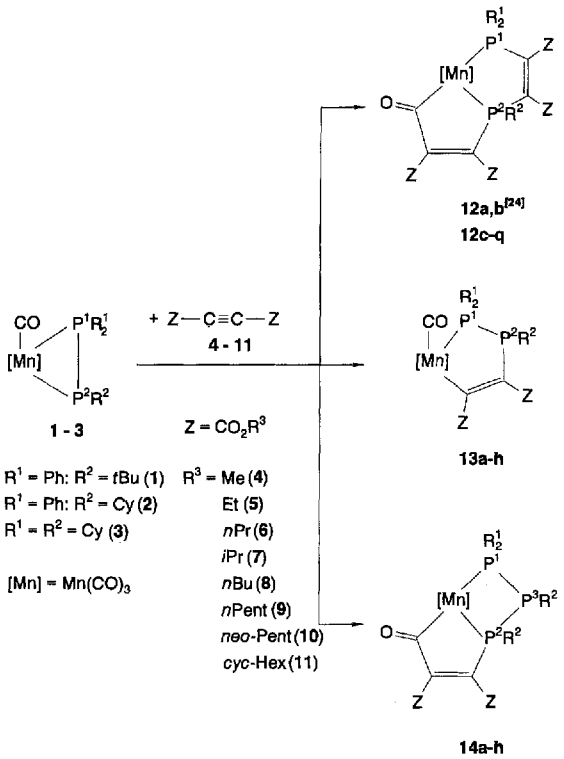
13a–c, e–h and **14a–c, e–h** were unequivocally detected $^{31}P\{^1H\}$-NMR spectroscopically. If the steric demand in the starting compound is released, the heterocycles **2** and **3** react with the alkynes **6–8, 10, 11**, and **6, 7, 10**, respectively, only to give the corresponding bicyclic species **12i–q**. The latter were not isolated either, but were characterized by their $^{31}P\{^1H\}$-NMR spectra. The corresponding diphosphamanganabicyclo[3.3.0]octadienones **12a, b** were described recently[24]. As their congeners **12a, b**, the octadienones **12c–h** are red-brown compounds which dissolve readily in polar and non-polar solvents. They are stable toward atmospheric oxygen in solution and in the solid state. In the field-desorption mass spectra of **12c–h** the expected molecular peak is observed.

Scheme 1



R^1	Ph	Ph	Ph	Ph	Ph	Ph	Ph	Ph	Ph
R^2	*t*Bu	*t*Bu	*t*Bu	*t*Bu	*t*Bu	*t*Bu	*t*Bu	*t*Bu	*cyc*-Hex
R^3	Me	Et	*n*Pr	*i*Pr	*n*Bu	*n*Pent	*neo*-Pent	*cyc*-Hex	*n*Pr
	a	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**

R^1	Ph	Ph	Ph	Ph	*cyc*-Hex	*cyc*-Hex	*cyc*-Hex
R^2	*cyc*-Hex	*cyc*-Hex	*cyc*-Hex	*cyc*-Hex	*cyc*-Hex	*cyc*-Hex	*cyc*-Hex
R^3	*i*Pr	*n*Bu	*neo*-Pent	*cyc*-Hex	*n*Pr	*i*Pr	*neo*-Pent
	k	**l**	**m**	**n**	**o**	**p**	**q**

The IR spectra of **12c–h** display only three CO absorptions in the 5-μm region, because one CO ligand is incorporated into the ring framework.

The existence of two doublets (P^1: $89.0 < \delta < 107$; P^2: $133.0 < \delta < 148.1$; see Experimental, Table 2) in the $^{31}P\{^1H\}$-NMR spectra of **12c–q** with far smaller coupling constants ($35.0 < {}^2J_{P^1P^2} < 41.2$ Hz; see Experimental, Table 2) than those observed in the spectra of the starting compounds **1–3** (P^1: $25.6 < \delta < 47.1$; P^2: $-138.3 < \delta < -192.0$; $438 < {}^1J_{P^1P^2} < 496$ Hz[23]) is consistent with the fact, that the alkynes were inserted into the P–P bonds of **1–3**. The transition of **1–3** to **12c–q** is accompanied by a remarkably downfield shift of both ^{31}P doublets which is even drastic in the case of P^2. Both phosphorus atoms (P^1 and P^2) are incorporated into one and two five-membered rings[26], respectively. Moreover, the coordination number of P^2 is increased from three to four.

In the $^{13}C\{^1H\}$-NMR spectra of the bicyclic compounds **12c–h** the signals of the ring carbon atoms can be separated into two groups. Due to the coupling with both phosphorus atoms at low field a doublet of doublets is observed which is assigned to the ring carbonyl function. In the middle region of the spectra the absorptions of the olefinic ring carbon atoms are found. Selectively ^{31}P-decoupled $^{13}C\{^1H\}$-NMR spectra enable the assignment of these ^{13}C signals. The carbon atoms of the terminal carbonyl ligands give rise to a multiplet at about $\delta = 220$.

Another type of compound, formed only in the reaction of the three-membered heterocycle **1** with the alkynes **4–11**, is the five-membered ring in **13a–h**. Since it is rather difficult to separate excess alkyne from **13a–h** by means of MPLC it was impossible to isolate these compounds in a pure form. In the case of **13d** we succeeded in eliminating most of the alkyne, and the prepurified products of several charges were collected and recrystallized at −78 °C from *n*-hexane. The field-desorption mass spectrum of the thermally stable compound **13d** which is soluble in polar and non-polar organic solvents shows the inclusion of only one alkyne molecule in **1**. A proof for the presence of intact P–P bonds in **13a–h** was furnished by the $^{31}P\{^1H\}$-NMR spectra. They reveal two doublets with coupling constants of approximately 280 Hz. Four intensive carbonyl bands in the 5-μm region of the IR spectrum of **13d** are in favor of the expected *cis*-$Mn(CO)_4$ arrangement.

Of particular interest are two signal groups in the $^{13}C\{^1H\}$-NMR spectrum of **13d**. At low field one observes four distinct resonances which are attributed to the carbon atoms of the four terminal carbonyl groups. Because of the ^{31}P couplings one resonance is split into a doublet and the two others into doublets of doublets. At higher field a broad singlet ($\delta = 165$) and a doublet of doublets ($\delta = 155$) are assigned to the ring carbon atoms Mn–C and P^2–C, respectively.

Byproducts of the reaction of **1** with the alkynes **4–11** are the red triphosphamanganabicyclo[3.2.0]heptenones **14a–h**. Only in the case of **14d** it was possible to isolate the heterocycle because the red solid precipitated from *n*-hexane. Because of the low yield the heterocycles **14a–c, e–h** could not be obtained in a pure form. **14d** is thermally stable and soluble in THF and halogenated hydrocarbons, but hardly soluble in non-polar solvents like *n*-hexane. In the field-desorption mass spectrum of **14d** the molecular

peak is in favor of the expected composition of the bicyclic heterocycle.

In the $^{31}P\{^1H\}$-NMR spectrum of **14d** three doublets of doublets are ascribed to three adjacent phosphorus atoms P^1, P^2, and P^3 (Scheme 1). Whereas the resonance of P^3 shows two large ^{31}P coupling constants because it is located between P^1 and P^2, the signals of the latter two phosphorus atoms are characterized by each one large and small coupling constant. In the metal carbonyl region of the IR spectrum of **14d** three intensive absorptions typical of a *fac*-$Mn(CO)_3$ arrangement occur. The fourth CO ligand is incorporated into the ring framework.

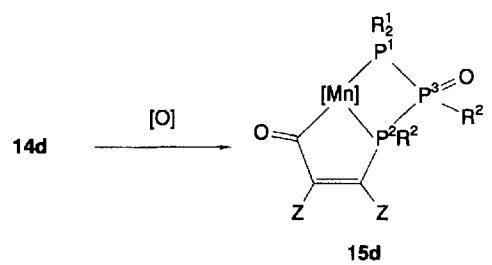
Although **12d** and **14d** contain the same ring fragment [Mn]−P^2R^2−CZ=CZ−C(O) the $^{13}C\{^1H\}$-NMR spectrum of **14d** is significantly different from that of **12d**. At δ = 220 a multiplet is found which is caused by the carbon atoms of the three terminal CO groups. At low field a doublet of doublets is attributed to the ring carbonyl C atom (δ = 251). The splitting is ascribed to the coupling with P^1 and P^2. Signals of the olefinic ring carbon atoms −(O)C−C(Z)= and $-R^2P^2-C(Z)=$ are observed at δ = 143 and 165, respectively. This assignment was evidenced by selective ^{31}P decoupling experiments.

Although both phosphorus atoms P^2 and P^3 in **14a−h** are chiral, no diastereomers were detected. Because of the steric encumbrance of the *t*Bu substituents at both P atoms which are included in a four-membered ring, the *trans* arrangement of these substituents is preferred and hence only one diastereomer is formed.

Attempts at hydrolytic or oxidative degradation of **14d** to give metal-free products failed. Upon refluxing a solution of **14d** in methanol with aqueous HCl **14d** remained unchanged. Oxidation of **14d** with $(NH_4)_2[Ce(NO_3)_6]$ led to a complete decomposition of the compound.

In the bicyclic compounds **14** the ring phosphorus atom P^3 shows the expected basic character which was demonstrated in the case of **14d**. Its reaction with 3-chloroperoxobenzoic acid in THF affords the corresponding red oxide **15d** (Scheme 2), which is readily soluble in THF and halogenated hydrocarbons. It is air-stable in solution and in the solid state. The field-desorption mass spectrum shows the expected molecular peak with high intensity. The signal patterns in the $^{13}C\{^1H\}$- and $^{31}P\{^1H\}$-NMR spectra of **15d** are comparable to those of the starting compound **14d** with the exception that the doublet of doublets of P^3 in the $^{31}P\{^1H\}$-NMR spectrum is shifted to low field which can be rationalized by the oxidation of this atom.

Scheme 2



The product spectrum of the reaction of the heterocycle **1** with the alkynes **4−11** depends on the polarity of the solvent as shown in the case of the alkynes **7** and **10**. In THF only the formation of the five-membered rings **13d, g** was observed (Scheme 1).

2) Molecular Structures of 14d and 15d

To prove the structures of the novel bicyclic compound **14d** and its oxygen-containing congener **15d** X-ray structure determinations were carried out (Figure 1). The octahedral geometry of **14d** and **15d** is distorted [e.g. P1−Mn1−P3 = 79.39(4) and 82.24(6)°, respectively]. Both heterocycles consist of a five- and four-membered ring which are connected by Mn1 and P1. Whereas the five-membered rings are nearly planar (angular sum 539°), the four-membered rings adopt a butterfly conformation. The interplanar angle of the two planes which are defined by the atoms P1, P2, P3 and Mn1, P1, P3 is 158.6 for **14d** and 162.0° for **15d**. The angle between the five-membered ring and the plane Mn1, P1, P3 is 100.1 and 100.0°, respectively. Compared to **14d**, the oxidation of P2 with oxygen leads to elongated P1−P2 and P1−P3 bonds.

3) Behavior of 1 Toward Lewis Acids

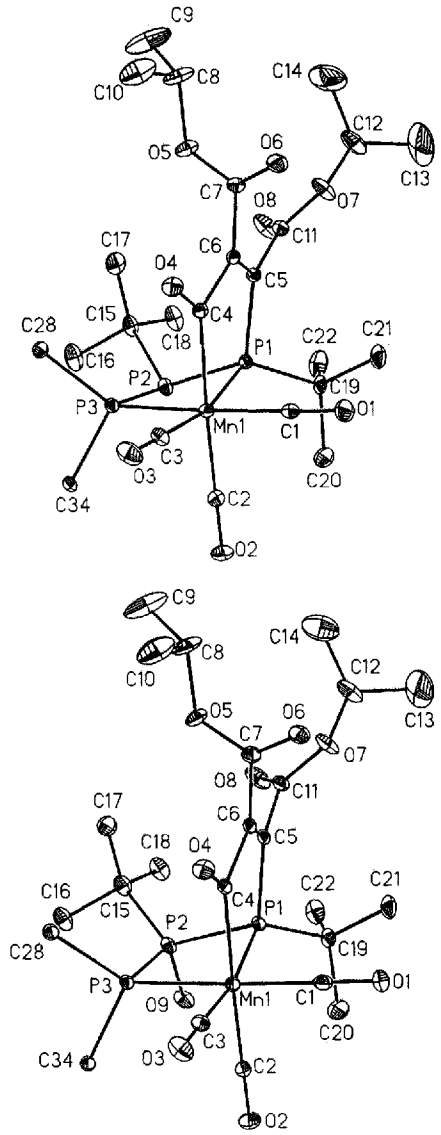
To study the basic character of the phosphorus atom P^2 in **1**, this heterocycle was treated with an equimolar amount of the THF-stabilized Lewis acid $THFCr(CO)_5$ in THF (Scheme 3). The yellow Lewis acid/Lewis base adduct **16** was purified by column chromatography. It is soluble in all common organic solvents and is air-sensitive in solution and in the solid state. A field-desorption mass spectrum revealing the molecular peak confirmed its composition. Two doublets of doublets with a large coupling constant in the $^{31}P\{^1H\}$-NMR spectrum of **16** are characteristic of a direct P−P contact. In the 5-μm region of the IR spectrum seven strong bands are observed for the terminal carbonyl groups which can be attributed to the *cis*-$Mn(CO)_4$ and $Cr(CO)_5$ moieties[27].

4) Reaction Mechanism

The mechanism of the reactions of the three-membered heterocycles **1−3** with the activated alkynes **4−11** may be rationalized by a nucleophilic attack of the phosphorus atom P^2 at one of the triply bonded carbon atoms of the alkyne as the first step (Scheme 4, **A**)[28,29]. Reactions of tertiary phosphanes with easily polarizable dialkyl acetylenedicarboxylates are well established[30]. The Lewis basic behavior of P^2 was also demonstrated by the addition of $THFCr(CO)_5$ to **1** (Scheme 3). The polar intermediate **A** is stabilized either by an insertion of the alkyne into the P^1-P^2 or into the Mn−P^2 bond. A further possibility for the stabilization of **A** is an intramolecular[24] or intermolecular nucleophilic attack of an alkyne carbon atom at a terminal carbonyl ligand of the same or of a different three-membered ring (Scheme 5, **D**).

Considering the above-mentioned remarks, the formation of the bicyclic compounds **12** may follow the reaction steps

Figure 1. ORTEP plots of the molecular structures of the bicyclic compounds **14d** (top) and **15d** (bottom). The phenyl groups at the phosphorus atoms P3 are omitted for clarity. – Selected bond lengths [pm] and angles [°] of **14d**: Mn–C(4) 204.9(3), Mn–P(1) 228.5(1), Mn–P(3) 233.2(1), P(1)–C(5) 183.5(3), C(4)–C(6) 153.3(4), C(5)–C(6) 133.0(4), P(1)–P(2) 219.7(2), P(2)–P(3) 221.1(1); P(1)–Mn–P(3) 79.39(4), Mn–P(3)–P(2) 95.16(5), P(1)–P(2)–P(3) 83.98(5), Mn–P(1)–P(2) 96.90(5), P(1)–Mn–C(4) 83.27(10). – **15d**: Mn–C(4) 204.8(4), Mn–P(1) 227.5(2), Mn–P(3) 233.5(2), P(1)–C(5) 183.6(4), C(4)–C(6) 154.5(6), C(5)–C(6) 132.7(5), P(1)–P(2) 224.7(2), P(2)–P(3) 227.2(2), P(2)–O(9) 149.1(3); P(1)–Mn–P(3) 82.24(6), Mn–P(3)–P(2) 93.98(6), P(1)–P(2)–P(3) 84.29(7), Mn–P(1)–P(2) 96.34(7), P(1)–Mn–C(4) 83.71(12)



depicted in Scheme 4. First of all the intermediate **A** is formed as already described which is stabilized by the insertion of the alkyne into the P^1-P^2 bond of **1**. In contrast to the corresponding diphosphamolybdacyclopentenes $[Mo]-P^1R_2^1-CZ=CZ-P^2R^2$ {[Mo] = $(\eta^5\text{-}C_5H_5)Mo(CO)_2$}[29], the manganese analogs could not be detected or even isolated. Obviously, the $Mn(CO)_4$ fragment is sterically less encumbering and hence the diphosphamanganacyclopentenes are kinetically less stable than their molybdenum congeners. The phosphorus atom P^2 of the manganese-containing five-membered intermediate immediately attacks another triply bonded alkyne carbon atom (Scheme 4, **B**); the second alkyne carbon atom concomitantly attacks in a nucleophilic manner a terminal carbonyl group of the $Mn(CO)_4$ moiety (**C**). The final products of these reaction sequences are the bicyclic compounds **12**.

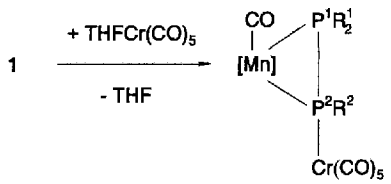
Concerning the formation of the bicyclic compounds **14** the first step is again a nucleophilic reaction of **1** with an alkyne (vide supra). In contrast to the formation of **12**, however, in that case the alkyne subsequently reacts intermolecularly with one terminal carbonyl ligand of another three-membered ring **1** (Scheme 5, **D**). A reorganization of several bonds and elimination of $[(OC)_4MnP^1R_2^1]_n$ finally result in the formation of **14** (**E** → **F** → **14**).

Table 1. Crystal data and refinement details for compounds **14d** and **15d**

	14d	**15d**
formula	$C_{34}H_{42}MnO_8P_3$	$C_{34}H_{42}MnO_9P_3$
M_r	726.53	742.53
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a [Å]	9.953(2)	10.027(5)
b [Å]	10.167(2)	10.170(5)
c [Å]	20.671(4)	20.682(9)
α [°]	97.49(4)	97.41(4)
β [°]	94.71(4)	93.93(4)
γ [°]	116.65(3)	116.51(3)
V [Å^3]	1830.1(6)	1853(2)
$\rho_{calcd.}$ [g cm^{-3}]	1.318	1.331
Z	2	2
$F(000)$ [e]	760	776
T [°C]	-100	-100
μ(Mo-K_α) [mm^{-1}]	0.538	0.535
scan mode	ω	ω
hkl range	±11, ±12, ±24	±11, ±12, −24→15
2θ limits [°]	4-50	4-50
measured refl.	12899	11871
observed refl. I>2δ(I)	4056	3972
refined parameters	416	425
S	1.218	1.387
$R1$[a]	0.04	0.05
$wR2$[b]	0.09	0.11

[a] $R1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$. –
[b] $wR2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Scheme 3



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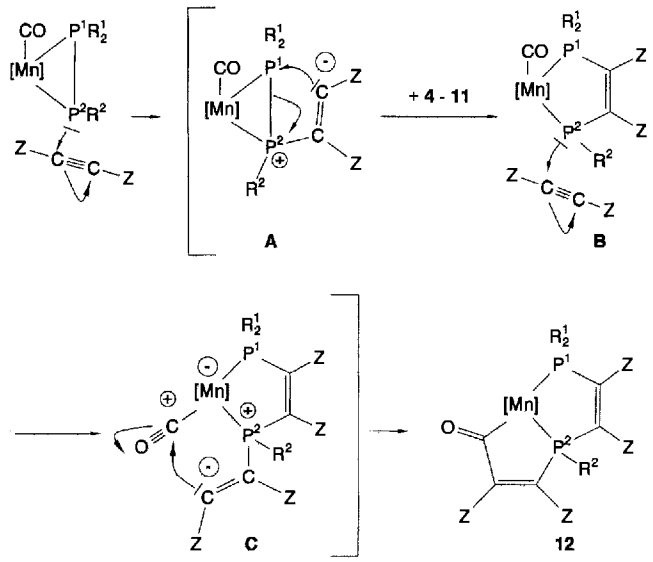
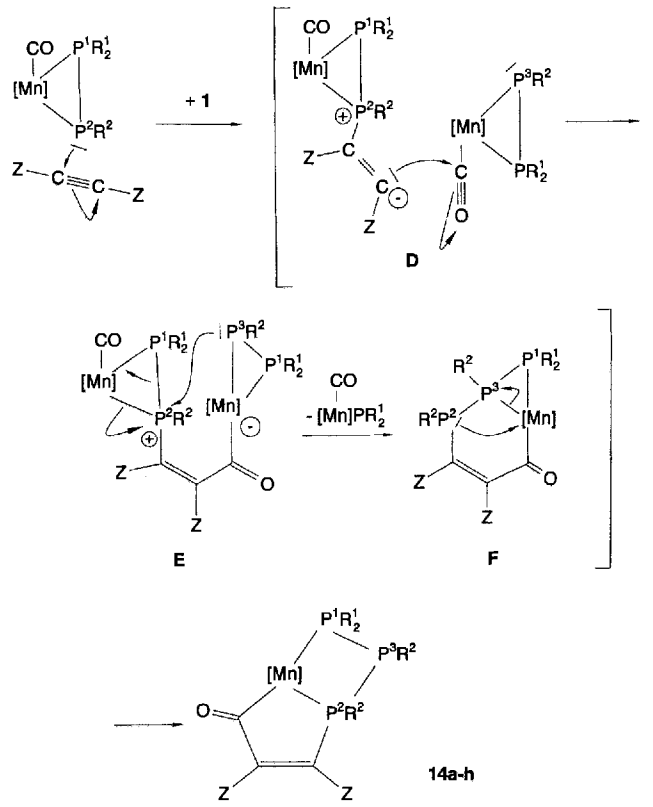
Scheme 4



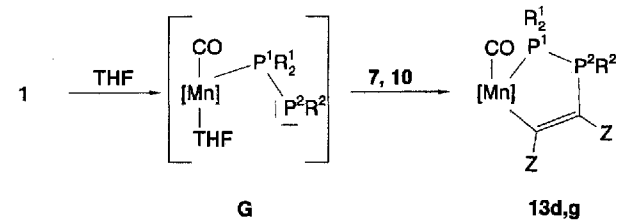
Scheme 5



5) Solvent and Steric Effects

The kind of the reaction products strongly depends on the polarity of the employed solvent. If the starting compound **1** is treated with the alkynes **4**–**11** in a non-polar solvent like *n*-hexane three different types of heterocycles are formed: the five-membered rings **13a**–**h**, the diphosphamanganabicyclo[3.3.0]octadienones **12a**–**h**, and the triphosphamanganabicyclo[3.2.0]heptenones **14a**–**h**. As already mentioned, in non-polar solvents the primary reaction step is the nucleophilic attack of P^2 of **1** at a triply bonded carbon atom of the activated alkyne. Subsequently, the alkyne may be inserted either into the P^1-P^2 or the $Mn-P^2$ bond of **1**, and another or the same alkyne attacks intra- or intermolecularly a terminal carbonyl group of a $Mn(CO)_4$ moiety. However, if the same reaction is carried out in THF, only the five-membered heterocycles **13** are formed. Possibly a solvent-stabilized intermediate **G** (Scheme 6) accounts for that different course of reaction. A similar intermediate is supposed to be responsible for the occurrence of the P-isomeric five-membered heterocycles $(OC)_4\overline{Mn-PR_2-S-CZ=CZ}$ (Z = CO_2R) in the cyclocotrimerization of thiophosphinites with electron-poor acetylenes in polar solvents like THF[31]. The next step is again a nucleophilic attack of P^2 at an alkyne carbon atom followed by a ring closure to give the heterocycles **13**. Hence, the formation of other reaction products is ruled out in that solvent.

Scheme 6



There is also a steric impact which controls the reaction pattern. To get more information about such effects the reaction of the starting compound **1** with the alkynes **4**–**11** containing differently substituted ester carbonyl functions was studied. Quantitative $^{31}P\{^1H\}$-NMR investigations (Experimental) allowed the determination of the ratio of the products **13a**–**h** and **12a**–**h**. In any case the yield of the triphosphamanganabicyclo[3.2.0]heptenones **14a**–**h** is too low to include them in this approach. The molar ratios of **13** to **12** were obtained by integration of the ^{31}P-NMR absorptions. In the case of R^3 = Me and Et the formation of **12** is somewhat preferred (**13**/**12** = 0.8). With increasing chain length (R^3 = *n*Pr, *n*Bu, *n*Pent) the product formation changes in favor of **13** (**13**/**12** = 1.2). If the alkyl group R^3 is branched in the α position (R^3 = *i*Pr, *cyc*-Hex) the ratio of **13** to **12** is increased to 1.6 and 1.5, respectively. Finally, if the R^3 substituent is branched at the β carbon atom (R^3 = *neo*-Pent) the ratio of **13**:**12** = 1.1 is nearly the same as in the case of R^3 = *n*Pent. The reactions of the heterocycles **2** and **3** bearing less sterically demanding substituents R^2 at the phosphorus atom P^2 with the activated alkynes **6**–**8**, **10**, and **11** in *n*-hexane lead only to the formation of the diphosphamanganabicyclo[3.3.0]octadienones **12i**–**q**. To sum up these results, it can be said that an increase in steric encumbrance either at the alkyne carbon atoms or at the phosphorus atom P^2 favors the formation of the five-membered rings **13**.

Conclusion

Recently, we could demonstrate[20,21] that, depending on the steric demand of the phosphorus-bound substituents R^1, activated alkynes are generally inserted into the M–P or into the M–S bond of three-membered heterocycles of the type $L_n\overline{M-PR^1_2-S}$ (M = Mn, Co, Ni). An insertion into the P–S bond succeeds only with phosphaalkynes[32]. The same reactivity may be anticipated if sulfur is replaced by an isolobal R^2P^2 function leading to the heterocycles $L_n\overline{M-P^1R^1_2-P^2R^2}$[24,25,27]. The course of the reaction being under consideration, however, is determined by the increased basicity of P^2 compared to the sulfur atom which is expressed by the already mentioned nucleophilic attack of this phosphorus atom at one of the alkyne carbon atoms. In contrast to the corresponding molybdenum compounds $\overline{[Mo]-P^1R^1_2-P^2R^2}$ {[Mo] = $(\eta^5\text{-}C_5H_5)Mo(CO)_2$}[29] offering only the P^1-P^2 bond for an alkyne insertion, the related manganese-containing derivatives $(OC)_4\overline{Mn-P^1R^1_2-P^2R^2}$ (**1**–**3**) are available for several reaction possibilities. This different behavior is attributed to the lower steric demand of the $Mn(CO)_4$ fragment. If the heterocycles $(OC)_4\overline{Mn-P^1R^1_2-P^2R^2}$ are sterically constrained as it is the case in **1** bulky acetylenes are rather inserted into the $Mn-P^2$ bond. Obviously, this bond is sterically less shielded than the P^1-P^2 bond. A further possibility of controlling the reaction arises from solvent effects.

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Experimental

All manipulations were carried out under argon by using standard Schlenk techniques. Solvents were dried with appropriate reagents and stored under argon. The starting compounds **1**–**3**[23] and the alkynes **4**–**11**[33,34] were prepared as described.

MS (FD): Finnigan MAT 711A modified by AMD (8 kV, 60°C). – IR: Bruker IFS 48. – ^{1}H NMR: Bruker AMX 400, AC 250 and DRX 250 at 400.14 and 250.13 MHz. – $^{13}C\{^1H\}$ NMR: Bruker AMX 400 and Bruker AC 250 at 100.61 and 62.90 MHz. The assignments of the aromatic carbon and hydrogen atoms and those of the higher aliphatic substituents are reported in ref.[35]. – $^{13}C\{^1H\}$ NMR (selective phosphorus decoupling experiments): Bruker AMX 400 at 100.61 MHz. – $^{31}P\{^1H\}$ NMR: Bruker WP 80 at 32.90 MHz, external standard 1% H_3PO_4 in [D_6]acetone and Bruker DRX 250 at 101.25 MHz. With the exception of the measurements with Bruker WP 80 chemical shifts were recorded relative to partially deuterated solvent peaks which are reported relative to tetramethylsilane. – Medium-pressure liquid chromatography (MPLC): Knauer HPLC Pumpe 64, UV Photometer, Merck Lobar Column C (550–37), LiChroprep Si 60 (40–63) – Microanalyses: Carlo Erba, model 1106 and AAS Perkin-Elmer, model 4000.

Determination of the Molar Product Ratio **13a–h/12a–h** *by Quantitative $^{31}P\{^1H\}$-NMR Spectroscopy:* In order to obtain an accurate integration of the $^{31}P\{^1H\}$-NMR signals inverse gated decoupling of the ^{1}H spins and a pulse delay of $>5T_1$ were applied[36]. To a solution of **1** (50 mg, 0.11 mmol) in 20 ml of *n*-hexane the corresponding alkyne (0.22 mmol) was added, and the solution was stirred at 20°C. After completion of the reaction, the solvent was removed and the crude residue dissolved in 0.4 ml of $CDCl_3$. This solution was investigated by quantitative $^{31}P\{^1H\}$-NMR spectroscopy.

1. *General Procedure for the Synthesis of the Heterocycles* **12c–q**, **13c–h**, *and* **14c–h**: To a solution of **1**–**3** in 50 ml of *n*-hexane the corresponding alkyne **4**–**11** was added, and the solution was stirred at 20°C. During this procedure the color changed from yellow to deep red. After removal of the solvent in vacuo the compounds **12c–h**, **13c–h**, and **14c–h** were prepurified by column chromatography [(10 × 2.5 cm), silica gel (Merck Si 60, 60–200 µm), ethyl acetate]. The products were collected, and the solvent was removed. **12c–h**, **13c–h** were separated from **14c–h** by MPLC (ethyl acetate/*n*-hexane, 1:5). The first yellow fraction contained **13c–h**, the second red fraction **12c–h**. Purification by MPLC had to be repeated. Compounds **12i–q**, **13a–c**, **e–h**, and **14a–c**, **e–h** were not isolated, but characterized by their $^{31}P\{^1H\}$-NMR spectra (Table 2).

Table 2. $^{31}P\{^1H\}$-NMR data of the heterocycles **12a–q**, **13a–h**, **14a–h**, **15d**, and **16** (32.90 MHz, THF): δ values, *J* (Hz)

	P^1	P^2	P^3	$^2J_{P1P2}$	$^1J_{P1P3}$	$^1J_{P2P3}$
12a[24],[a]	90.5	146.1		35.0		
12b[24],[a]	90.8	147.1		35.0		
12c	89.5	146.8		35.6		
12d	89.0	147.0		36.5		
12e	89.7	146.9		35.3		
12f	89.6	146.7		35.9		
12g	90.4	148.1		36.6		
12h	89.0	146.6		36.3		
12i	93.3	131.3		40.4		
12k	92.8	132.0		41.2		
12l	93.8	131.4		40.4		
12m	92.5	130.8		40.5		
12n	92.6	132.0		41.0		
12o	105.4	131.1		39.3		
12p	105.4	132.8		39.6		
12q	107.0	133.0		39.5		
13a[b]	6.7	-15.2		283.6		
13b[b]	6.2	-15.4		284.0		
13c	7.0	-14.8		284.5		
13e	7.0	-14.7		284.7		
13f	7.0	-14.7		284.5		
13g	5.3	-15.5		279.7		
13h	4.7	-16.1		277.9		
14a[b]	15.3	86.2	52.0	25.3	280.2	199.7
14b[b]	15.6	86.8	52.7	26.9	279.0	199.6
14c	16.2	87.4	51.9	25.2	279.4	198.8
14d	14.9	86.5	53.3	26.4	280.7	198.5
14e	15.8	86.5	52.4	26.8	279.5	198.3
14f	15.6	86.7	52.2	26.2	281.1	199.4
14g	15.3	85.4	52.7	25.7	279.4	198.9
14h	15.2	85.9	52.4	26.3	281.9	198.6
15d	51.9	127.4	149.0	57.9	150.6	174.8
16	24.9	-65.6		430.4		

[a] $CHCl_3$. – [b] 101.25 MHz, $CDCl_3$.

1.1. *Tetrapropyl 1-tert-Butyl-5,5,5-tricarbonyl-6-oxo-4,4-diphenyl-1λ⁴,4λ⁴-diphospha-5-manganabicyclo[3.3.0]octa-2,7-diene-2,3,7,8-tetracarboxylate* (**12c**): A solution of **1** (200 mg, 0.51 mmol) was

allowed to react within 2 h with **6** (500 mg, 2.53 mmol) to give 53 mg (12.4%) of **12c**, m.p. 93–94°C (dec.). – MS (FD), *m/z*: 836.6 [M^+]. – IR (KBr): $\tilde{\nu}$ = 2015, 1949, 1922 cm^{-1} (C≡O). – ^1H NMR (250.13 MHz, $CDCl_3$): δ = 1.10 (m_c, 20H, CH_2CH_3), 1.45 [d, $^3J_{PH}$ = 19.2 Hz, 9H, $C(CH_3)_3$], 3.85 [m_c, 8H, $C(O)CH_2$]. – $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ = 143.00 [d, $^2J_{PC}$ = 14.2 Hz, P²C=*C*C(O)], 151.90 (dd, $^1J_{PC}$ = 31.9, $^2J_{PC}$ = 22.2 Hz, P²*C*=CP¹), 156.49 (dd, $^1J_{PC}$ = 31.2, $^2J_{PC}$ = 11.7 Hz, P²C=*C*P¹), 160.56 [dd, $^1J_{PC}$ = 34.7, $^3J_{PC}$ = 4.2 Hz, P²*C*=CC(O)], 218.97 (m_c, C≡O), 269.06 [dd, $^2J_{PC}$ = 17.3, $^2J_{PC}$ = 9.4 Hz, Mn*C*(O)C=]. – $C_{40}H_{47}MnO_{12}P_2$ (836.7): calcd. C 57.42, H 5.66, Mn 6.57; found C 57.21, H 5.52, Mn 6.13.

1.2. *Tetraisopropyl 1-tert-Butyl-5,5,5-tricarbonyl-6-oxo-4,4-diphenyl-1λ⁴,4λ⁴-diphospha-5-manganabicyclo[3.3.0]octa-2,7-diene-2,3,7,8-tetracarboxylate* (**12d**): A solution of **1** (245 mg, 0.55 mmol) was allowed to react within 2 h with **7** (550 mg, 2.77 mmol) to give 115 mg (25.0%) of **12d**, m.p. 62–63°C (dec.). – MS (FD), *m/z*: 836.6 [M^+]. – IR (KBr): $\tilde{\nu}$ = 2014, 1946, 1924 cm^{-1} (C≡O). – ^1H NMR (250.13 MHz, $CDCl_3$): δ = 0.59 (d, $^3J_{HH}$ = 6.0 Hz, 3H, $CHCH_3$), 0.69 (d, $^3J_{HH}$ = 6.0 Hz, 3H, $CHCH_3$), 1.06 [d, $^3J_{HH}$ = 4.7 Hz, 6H, $CH(CH_3)_2$], 1.22 [t, $^3J_{HH}$ = 4.8 Hz, 6H, $CH(CH_3)_2$], 1.30 [t, $^3J_{HH}$ = 4.7 Hz, 6H, $CH(CH_3)_2$], 1.46 [d, $^3J_{PH}$ = 17.0 Hz, 9H, $C(CH_3)_3$], 4.55 [m_c, 1H, $CH(CH_3)_2$], 4.78 [m_c, 1H, $CH(CH_3)_2$], 5.02 [m_c, 1H, $CH(CH_3)_2$], 5.13 (m_c, 1H, $CH(CH_3)_2$]. – $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ = 142.61 [d, $^2J_{PC}$ = 14.9 Hz, P²C=*C*C(O)], 151.90 (dd, $^1J_{PC}$ = 31.9, $^2J_{PC}$ = 22.2 Hz, P²*C*=CP¹), 156.49 (dd, $^1J_{PC}$ = 31.2, $^2J_{PC}$ = 11.7 Hz, P²C=*C*P¹), 160.56 [dd, $^1J_{PC}$ = 34.7, $^3J_{PC}$ = 4.2 Hz, P²*C*=CC(O)], 219.20 (m_c, C≡O), 269.06 [dd, $^2J_{PC}$ = 17.3, $^2J_{PC}$ = 9.4 Hz, Mn*C*(O)C=]. – $C_{40}H_{47}MnO_{12}P_2$ (836.7): calcd. C 57.42, H 5.66, Mn 6.57; found C 57.30, H 5.98, Mn 6.59.

1.3. *Tetrabutyl 1-tert-Butyl-5,5,5-tricarbonyl-6-oxo-4,4-diphenyl-1λ⁴,4λ⁴-diphospha-5-manganabicyclo[3.3.0]octa-2,7-diene-2,3,7,8-tetracarboxylate* (**12e**): A solution of **1** (220 mg, 0.50 mmol) was allowed to react within 2 h with **8** (565 mg, 2.50 mmol) to give 56 mg (12.6%) of **12e**, m.p. 79°C (dec.). – MS (FD), *m/z*: 892.6 [M^+]. – IR (KBr): $\tilde{\nu}$ = 2021, 1961, 1930 cm^{-1} (C≡O). – ^1H NMR (250.13 MHz, $CDCl_3$): δ = 1.05 (m_c, 28H, $CH_2CH_2CH_3$), 1.46 [d, $^3J_{PH}$ = 17.1 Hz, 9H, $C(CH_3)_3$], 3.80 [m_c, 8H, $C(O)CH_2$]. – $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ = 142.98 [d, $^2J_{PC}$ = 12.9 Hz, P²C=*C*C(O)], 152.57 (dd, $^1J_{PC}$ = 31.7, $^2J_{PC}$ = 22.4 Hz, P²*C*=CP¹), 155.40 (dd, $^1J_{PC}$ = 31.7, $^2J_{PC}$ = 11.5 Hz, P²C=*C*P¹), 164.47 [dd, $^1J_{PC}$ = 34.9, $^3J_{PC}$ = 4.1 Hz, P²*C*=CC(O)], 219.18 (m_c, C≡O), 268.57 [dd, $^2J_{PC}$ = 17.2, $^2J_{PC}$ = 9.7 Hz, Mn*C*(O)C=]. – $C_{44}H_{55}MnO_{12}P_2$ (892.8): calcd. C 59.19, H 6.21, Mn 6.15; found C 58.77, H 6.26, Mn 5.87.

1.4. *Tetrapentyl 1-tert-Butyl-5,5,5-tricarbonyl-6-oxo-4,4-diphenyl-1λ⁴,4λ⁴-diphospha-5-manganabicyclo[3.3.0]octa-2,7-diene-2,3,7,8-tetracarboxylate* (**12f**): A solution of **1** (250 mg, 0.57 mmol) was allowed to react within 2 h with **9** (725 mg, 2.85 mmol) to give 73 mg (13.5%) of **12f**, m.p. 61°C (dec.). – MS (FD), *m/z*: 948.2 [M^+]. – IR (KBr): $\tilde{\nu}$ = 2016, 1950, 1929 cm^{-1} (C≡O). – ^1H NMR (250.13 MHz, $CDCl_3$): δ = 1.10 (m_c, 36H, $CH_2CH_2CH_2CH_3$), 1.46 [d, $^3J_{PH}$ = 17.0 Hz, 9H, $C(CH_3)_3$], 3.90 [m_c, 8H, $C(O)CH_2$]. – $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ = 142.89 [d, $^2J_{PC}$ = 14.3 Hz, P²C=*C*C(O)], 151.78 (dd, $^1J_{PC}$ = 31.1, $^2J_{PC}$ = 22.9 Hz, P²*C*=CP¹), 156.63 (dd, $^1J_{PC}$ = 31.8, $^2J_{PC}$ = 11.4 Hz, P²C=*C*P¹), 161.22 [dd, $^1J_{PC}$ = 34.1, $^3J_{PC}$ = 4.3 Hz, P²*C*=CC(O)], 218.94 (m_c, C≡O), 269.06 [dd, $^2J_{PC}$ = 17.3, $^2J_{PC}$ = 9.4 Hz, Mn*C*(O)C=]. – $C_{48}H_{63}MnO_{12}P_2$ (948.9): calcd. C 60.76, H 6.69, Mn 5.79; found C 60.58, H 6.72, Mn 5.55.

1.5. *Tetraneopentyl 1-tert-Butyl-5,5,5-tricarbonyl-6-oxo-4,4-diphenyl-1λ⁴,4λ⁴-diphospha-5-manganabicyclo[3.3.0]octa-2,7-diene-2,3,7,8-tetracarboxylate* (**12g**): A solution of **1** (220 mg, 0.5 mmol) was allowed to react within 2 h with **10** (1.27 g, 2.50 mmol) to give 105 mg (22.2%) of **12g**, m.p. 67°C (dec.). – MS (FD), *m/z*: 948.6 [M^+]. – IR (KBr): $\tilde{\nu}$ = 2016, 1949, 1919 cm^{-1} (C≡O). – ^1H NMR (400.14 MHz, $CDCl_3$): δ = 0.48, [s, 9H, $C(CH_3)_3$], 0.78 [s, 9H, $C(CH_3)_3$], 0.87 [s, 9H, $C(CH_3)_3$], 0.78 [s, 9H, $C(CH_3)_3$], 1.47 [d, $^3J_{PH}$ = 17.0 Hz, 9H, $C(CH_3)_3$], 3.13 [d, $^2J_{HH}$ = 10.6 Hz, 1H, $CH_aH_bC(CH_3)_3$], 3.40 (d, $^2J_{HH}$ = 10.6 Hz, 1H, $CH_aH_bC(CH_3)_3$], 3.56 [d, $^2J_{HH}$ = 10.3 Hz, 1H, $CH_aH_bC(CH_3)_3$], 3.67 [d, $^2J_{HH}$ = 10.3 Hz, 1H, $CH_aH_bC(CH_3)_3$], 3.74 [d, $^2J_{HH}$ = 10.5 Hz, 1H, $CH_aH_bC(CH_3)_3$], 3.78 [d, $^2J_{HH}$ = 10.5 Hz, 1H, $CH_aH_bC(CH_3)_3$], 3.84 [d, $^2J_{HH}$ = 10.5 Hz, 1H, $CH_aH_bC(CH_3)_3$], 3.92 [d, $^2J_{HH}$ = 10.5 Hz, 1H, $CH_aH_bC(CH_3)_3$]. – $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ = 143.03 [d, $^2J_{PC}$ = 11.2 Hz, P²C=*C*C(O)], 152.37 (dd, $^1J_{PC}$ = 34.7, $^2J_{PC}$ = 22.4 Hz, P²*C*=CP¹), 155.61 (dd, $^1J_{PC}$ = 32.1, $^2J_{PC}$ = 12.8 Hz, P²C=*C*P¹), 160.39 [dd, $^1J_{PC}$ = 33.7, $^3J_{PC}$ = 4.2 Hz, P²*C*=CC(O)], 219.25 (m_c, C≡O), 269.54 [dd, $^2J_{PC}$ = 17.3, $^2J_{PC}$ = 9.4 Hz, Mn*C*(O)C=]. – $C_{48}H_{63}MnO_{12}P_2$ (948.9): calcd. C 60.76, H 6.69, Mn 5.79; found C 60.45, H 6.61, Mn 5.83.

1.6. *Tetracyclohexyl 1-tert-Butyl-5,5,5-tricarbonyl-6-oxo-4,4-diphenyl-1λ⁴,4λ⁴-diphospha-5-manganabicyclo[3.3.0]octa-2,7-diene-2,3,7,8-tetracarboxylate* (**12h**): A solution of **1** (310 mg, 0.70 mmol) was allowed to react within 2 h with **11** (980 mg, 3.50 mmol) to give 110 mg (15.8%) of **12h**, m.p. 98°C (dec.). – MS (FD), *m/z*: 997.6 [M^+]. – IR (KBr): $\tilde{\nu}$ = 2014, 1949, 1921 cm^{-1} (C≡O). – ^1H NMR (250.13 MHz, $CDCl_3$): δ = 1.40 [m_c, 40H, $C(O)CHCH_2CH_2CH_2CH_2CH_2$], 1.51 [d, $^3J_{PH}$ = 16.9 Hz, 9H, $C(CH_3)_3$], 4.43 [m_c, 1H, C(O)CH], 4.59 [m_c, 1H, C(O)CH], 4.83 [m_c, 1H, C(O)CH], 4.97 [m_c, 1H, C(O)CH]. – $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ = 142.86 [d, $^2J_{PC}$ = 13.5 Hz, P²C=*C*C(O)], 151.68 (dd, $^1J_{PC}$ = 31.2, $^2J_{PC}$ = 22.6 Hz, P²*C*=CP¹), 156.55 (dd, $^1J_{PC}$ = 31.5, $^2J_{PC}$ = 11.2 Hz, P²C=*C*P¹), 160.78 [dd, $^1J_{PC}$ = 34.1, $^3J_{PC}$ = 4.0 Hz, P²*C*=CC(O)], 219.21 (m, C≡O), 269.06 [dd, $^2J_{PC}$ = 17.3, $^2J_{PC}$ = 9.4 Hz, Mn*C*(O)C=]. – $C_{52}H_{63}MnO_{12}P_2$ (997.0): calcd. C 62.65, H 6.37, Mn 5.51; found C 62.58, H 6.15, Mn 5.75.

2. *Diisopropyl 1-tert-Butyl-3,3,3,3-tetracarbonyl-2,2-diphenyl-1,2λ⁴-diphospha-3-manganacyclopent-4-ene-4,5-dicarboxylate* (**13d**): As described in the General Procedure, three separate solutions of **1** (350 mg, 0.80 mmol; 400 mg, 0.91 mmol; 440 mg, 1.0 mmol) each in 50 ml of *n*-hexane were allowed to react within 2 h with **7** (793 mg, 4.0 mmol; 900 mg, 4.55 mmol; 990 mg, 5.0 mmol). The solvent was removed in vacuo, and each residue was purified by column chromatography and MPLC. The first yellow fractions were collected and again purified by means of MPLC (ethyl acetate/*n*-hexane, 1:5). Compound **13d** was found in the first fraction and recrystallized from *n*-hexane at –78°C. Yield 115 mg (6.6%) of **13d**, m.p. 112°C (dec.). – MS (FD), *m/z*: 637.9 [M^+]. – IR (KBr): $\tilde{\nu}$ = 2068, 1997, 1978, 1959 cm^{-1} (C≡O). – ^1H NMR (250.13 MHz, $CDCl_3$): δ = 0.81 (s, 3H, $CHCH_3$), 0.84 (s, 3H, $CHCH_3$), 1.08 (s, 3H, $CHCH_3$), 1.15 (s, 3H, $CHCH_3$), 1.24 [d, $^3J_{PH}$ = 11.0 Hz, 9H, $C(CH_3)_3$], 4.85 [m_c, 1H, C(O)CH], 5.03 [m_c, 1H, C(O)CH]. – $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ = 155.16 (dd, $^1J_{PC}$ = 40.3, $^2J_{PC}$ = 6.0 Hz, P²C=), 164.25 (s, br., P²C=*C*), 204.23 (dd, $^2J_{PC}$ = 10.3, $^3J_{PC}$ = 3.9 Hz, C≡O), 208.87 (d, $^2J_{PC}$ = 14.2, C≡O), 214.01 (dd, $^2J_{PC}$ = 13.6, $^3J_{PC}$ = 1.3 Hz, C≡O), 216.31 (s, C≡O). – $C_{30}H_{33}MnO_8P_2$ (638.5): calcd. C 54.64, H 5.60, Mn 8.60; found C 54.89, H 5.91, Mn 8.25.

3. *Diisopropyl 1,7-Di-tert-butyl-5,5,5-tricarbonyl-4-oxo-6,6-diphenyl-1λ⁴,6λ⁴,7-triphospha-5-manganabicyclo-[3.2.0]hept-2-ene-2,3-dicarboxylate* (**14d**): A solution of **1** (245 mg, 0.55 mmol) was allowed to react within 2 h with **7** (550 mg, 2.77 mmol). Compound **14d** precipitated from *n*-hexane and was filtered off (D4). The residue was washed with *n*-pentane (3 × 10 ml) and recrystallized from THF. Yield 105 mg (29.0%) of **14d**, m.p. 233°C. – MS (FD), *m/z*: 726.8 [M⁺]. – IR (CCl_4): $\tilde{\nu}$ = 2018, 1951, 1935 cm^{-1} (C≡O). – ^1H NMR (250.13 MHz, $CDCl_3$): δ = 1.19 [d, $^3J_{P^2H}$ = 18.6 Hz, 9H, $C(CH_3)_3$], 1.30 [s, 12H, $CH(CH_3)_2$], 1.38 [d, $^3J_{P^3H}$ = 16.0 Hz, 9H, $C(CH_3)_3$], 5.11 [m_c, 2H, C(O)CH]. – $^{13}C\{^1H\}$ NMR (100.61 MHz, [D₆]acetone): δ = 144.64 (s, $P^2C=C$), 164.44 (d, $^1J_{P^2C}$ = 32.9 Hz, $P^2C=$), 220.73 (m_c, C≡O), 250.67 [dd, $^2J_{P^1C}$ = 17.0, $^2J_{P^2C}$ = 9.5 Hz, $MnC(O)C=$]. – $C_{34}H_{42}MnO_8P_3$ (726.5): calcd. C 56.21, H 5.83, Mn 6.57; found C 55.82, H 5.98, Mn 6.59.

4. *Diisopropyl 1,7-Di-tert-butyl-5,5,5-tricarbonyl-4-oxo-6,6-diphenyl-1λ⁴,6λ⁴,7-triphospha-5-manganabicyclo[3.2.0]-hept-2-ene-2,3-dicarboxylate 7-Oxide* (**15d**): To a solution of **14d** (110 mg, 0.15 mmol) in 20 ml of THF 50 mg (0.30 mmol) of 3-chloroperoxobenzoic acid was added. After stirring of the mixture for 2 h at 20°C the solvent was removed in vacuo. The residue was treated with 10 ml of *n*-pentane and separated by filtration (D4), washed (3 × 10 ml of *n*-pentane), and recrystallized from THF. Yield 95 mg (84.5%), m.p. 214°C. – MS (FD), *m/z*: 742.0 [M⁺]. – IR (CCl_4): $\tilde{\nu}$ = 2012, 1953, 1920 cm^{-1} (C≡O). – ^1H NMR (250.13 MHz, $CDCl_3$): δ = 1.09 [d, $^3J_{P^2H}$ = 18.2 Hz, 9H, $C(CH_3)_3$], 1.30 [s, 12H, $CH(CH_3)_2$], 1.57 [d, $^3J_{P^3H}$ = 16.9 Hz, 9H, $C(CH_3)_3$], 5.17 [m_c, 2H, C(O)CH]. – $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ = 142.83 (s, $P^2C=C$), 165.22 (d, $^1J_{P^2C}$ = 35.2 Hz, $P^2C=$), 218.32 (m_c, C≡O), 273.92 [dd, $^2J_{P^1C}$ = 17.0, $^2J_{P^2C}$ = 9.5 Hz, $MnC(O)C=$]. – $C_{34}H_{42}MnO_9P_3$ (742.5): calcd. C 55.00, H 5.70, Mn 7.40; found C 55.12, H 6.00, Mn 7.56.

5. *Reaction of* **1** *with* **7** *and* **10** in THF: To a stirred solution of **1** (100 mg, 0.23 mmol) in 50 ml of THF the alkynes **7** (140 mg, 0.71 mmol) and **10** (180 mg, 0.71), respectively, were added. After a reaction time of 4 h only the signals of **13d, g**, were detected ^{31}P-NMR spectroscopically.

6. *2-tert-Butyl-3,3,3,3-tetracarbonyl-2-(pentacarbonylchromio)-1,1-diphenyl-1,2-diphospha-3-manganacyclopropane* (**16**): To a stirred solution of 350 mg (0.8 mmol) of **1** in 20 ml of THF a solution of $THFCr(CO)_5$, prepared by photolysis of 220 mg (1.0 mmol) of $Cr(CO)_6$ in 100 ml of THF[37], was added within 1 h at 20°C, and the mixture was stirred for 1 h. The solvent was removed in vacuo and the residue purified by column chromatography (basic alumina, 30 × 2.5 mm, *n*-hexane/diethyl ether, 5:1). Product **16** was isolated from the first yellow fraction. Yield 450 mg (71.2%), m.p. 121°C (dec.). – MS (FD), *m/z*: 632.0 [M⁺]. – IR (KBr): $\tilde{\nu}$ = 2072, 2051, 2006, 1981, 1965, 1941, 1935 cm^{-1} (C≡O). – $C_{25}H_{28}CrMnO_9P_2$ (631.9): calcd. C 47.49, H 3.03, Cr 8.22, Mn 8.69; found C 47.35, H 2.92, Cr 7.85, Mn 8.47.

Crystal Structure Determinations: Single crystals were obtained by slow diffusion of *n*-pentane into concentrated THF solutions of **14d** and **15d**, respectively. Crystals were mounted on a glass fiber and transferred to a P4 Siemens diffractometer by taking rotation photographs to find a suitable reduced cell (graphite-monochromated Mo-K_α radiation). The final cell parameters and specific data collection parameters are compiled in Table 1. All structures were solved by Patterson methods[38] and refined by the least-squares method with anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atoms were included in calculated positions (riding model). An absorption correction (ψ scan) was applied to all data. Maximum and minimum peaks in the final difference synthesis were 0.646 and −0.334 (**14d**), 0.688 and −0.617 (**15d**) eÅ^{-3}. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-59048, the names of the authors, and the journal citation.

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