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PHOSPHAHYDROQUINONES AND OXAPHOSPHOLES VIA CARBENE ANNULATION AND CYCLOADDITION REACTIONS OF CHROMIUM CARBONYL CARBENE COMPLEXES AND PHOSPHAALKYNES[1)]

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Abstract - Fischer-type alkoxy(aryl or vinyl)carbene complexes of chromium undergo regiospecific carbene annulation and cycloaddition upon reaction with *tert.*butyl phosphaacetylene to give highly substituted phosphahydroquinones and/or oxaphospholes. The product distribution is governed by steric and electronic effects arising from the substitution pattern in the carbene ligand. The phosphaannulation products such as phosphabenzene, -naphthalene, -benzofuran, -benzothiophene and -phenanthrene skeletons as well as the 1,3-oxaphospholes are obtained in yields up to 89% and - in part - are characterized by X-ray diffraction.

Soon after their discovery in 1964[3)] Fischer type carbene complexes $[(CO)_5M{=}C(R)R']$ turned out to gain considerable potential in organic synthesis[4)]. The interaction of a low-valent transition metal such as Cr°, Mo° or W° and pronounced acceptor coligands renders the carbene carbon a strongly electrophilic center[5)]. This is in accord with the isolobal analogy of the metal carbonyl fragment and an oxygen atom[6)], and has led to the description of these complexes as "metal-tuned carbonyl compounds"[7)]. Their chemical behaviour is in distinct contrast to that of complexes introduced by Schrock in 1974[8)] which are characterized by a reversed polarity of the metal-carbene bond ("metal-tuned ylides") resulting from the combination of a higher-valent metal center and efficient donor coligands[9)] Whereas Schrock-type compounds are mainly used as well-defined catalysts in olefin metathesis and ROMP reactions[10)], Fischer type complexes have become valuable reagents for stoichiometric carbon-carbon bond formation[4)].

BACKGROUND

The application of Fischer type carbene complexes in organic synthesis is based on two grounds: In one respect the metal-carbene unit may act as a novel functional group. As a consequence of the electrophilic carbene carbon adjacent C-H bonds exhibit an enhanced acidity; metal carbene "enolates" obtained by

α-deprotonation have been used in diastereoselective aldol and Michael reactions[11,12]. Similarly, α,ß-unsaturated carbene ligands are activated towards cycloaddition; for instance, Diels-Alder and Pauson-Khand reactions proceed at distinctly milder conditions than with the corresponding organic carbonyl analogues[13,14]. In all these reactions the metal-carbene bond is unaffected, and thus can be subsequently modified by nucleophilic addition or oxidative cleavage.

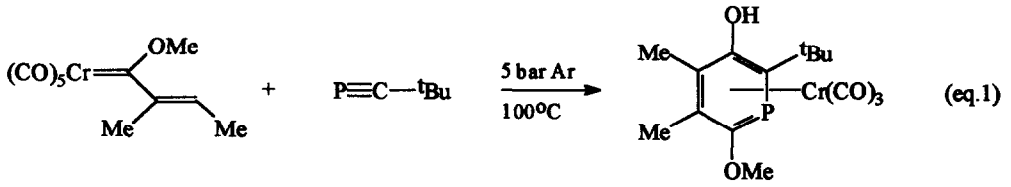
On the other hand, the low-valent metal center is able to act as a template at which one pot cycloaddition patterns unprecedented in organic chemistry may be set up. Typical examples are the chromium-mediated three component cycloaddition reactions which in a [4+2+1-2] mode lead to cyclopentenones[15] or in a [3+2+1] carbene annulation afford oxygenated arenes[16] The latter process in which an alkyne, an α,ß-unsaturated carbene and a carbonyl ligand are connected in a highly chemo- and regioselective manner has been increasingly used in the synthesis of natural products containing fused ring systems during the past decade[17] The benzannulation proceeds under mild conditions and is compatible with alkenyl-, aryl- and five-membered heteroaryl carbene ligands as well as with terminal and internal alkyl- and arylalkynes. The reaction fails with nucleophilic alkynes such as ynamines which - in competition with the required η^2-side on-coordination to the metal - primarily add directly to the carbene carbon atom and finally undergo insertion into the metal-carbene bond[18]. A similar addition/insertion sequence is observed for nitriles[19], the resulting iminocarbene complexes which are also accessible from alkoxycarbene complexes and imines or from aminocarbene precursors[20] have been shown to undergo a competitive [3+2+1] carbene annulation to 3-hydroxypyridines and [3+2] cycloaddition to pyrroles upon reaction with alkynes[20, 21]; the chemoselectivity is controlled by the substitution pattern both in the imino side chain and in the alkyne, and further seems to depend on the solvent used. An independent access to the pyridine skeleton is based on a formal [4+2] cycloaddition of alkynes to *Z*-ß-(monoalkylamino)vinylcarbene ligands[22].

The development of kinetically stabilized phosphaalkynes[23] - the higher homologues of nitriles - prompted us to investigate whether the carbene annulation methodology can be extended to heteroannulation using the P≡C bond as a heteroalkyne equivalent. We were encouraged by previous results from the coordination chemistry of phosphaalkynes which - towards low-valent metal centers - generally prefer an η^2-side on-coordination of the P≡C bond over an η^1-end on-coordination of the phosphorous lone pair[24] The chemical similarity of alkynes and phosphaalkynes is further documented by common metal-induced cyclooligomerization[24] and insertion reactions into metal-alkyl and metal-carbene bonds[25]. In this paper we present another analogy of these two classes of compounds which is based on carbene annulation and cycloaddition reactions leading to phosphahydroquinone and oxaphosphole structures[26].

CARBENE ANNULATION REACTIONS

Extending previous work on the benzannulation of vinylcarbene complexes[27] we turned to the (*E*)-2-butenylcarbene complex **1a** which was reacted with *tert.* butylphosphaacetylene **2**[28], a stable compound which is easy to handle. After warming a ^{t}BuOMe solution under 5 bar Ar to 100° for 2 h ^{31}P-NMR monitoring of the reaction indicated a signal compatible with a coordinated double-bound sp^2 phosphorous center; in addition, the IR spectrum confirmed the formation of a $Cr(CO)_3$ complex. Although

the yield was extremely low, chromatographic work-up and recrystallization afforded yellow crystals of **3** (eq. 1). Their X-ray analysis revealed that the expected phosphaannulation product had indeed formed containing a phosphinine ring which is coordinated to the $Cr(CO)_3$-fragment via its π-system (fig. 1). The geometry of the heterocyclic ligand resembles that of its 2,4,6-triphenylphosphinine congener[29], even though in **3** the alternating bond lengths between the ring atoms and the ring-puckering are more evident.



1a **2** **3**

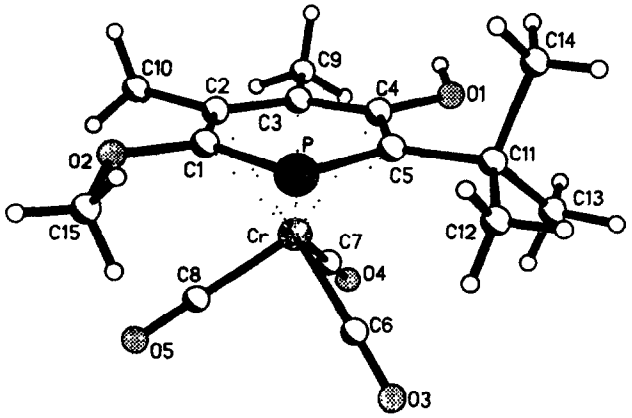
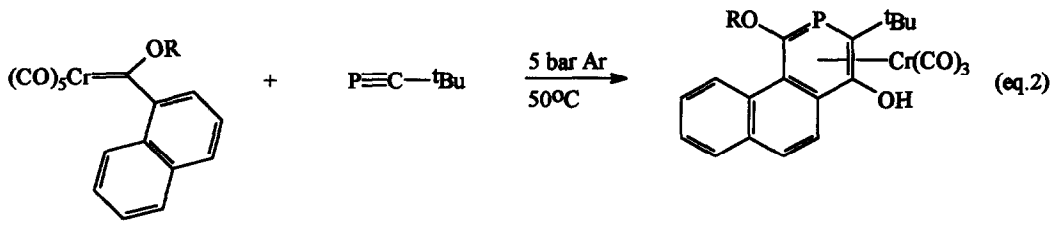


Fig. 1. Molecular structure of **3**. Selected bond lengths (Å) and angles (°): Cr-P 2.460(1),, Cr-C_{ring} 2.274(2) (average), Cr-$C_{carbonyl}$ 1.837(2) (average), P-C1 1 761(2), P-C5 1.780(2), C1-C2 1.420(3), C2-C3 1.413(2), C3-C4 1.433(2), C4-C5 1.404(3); C1-P-C5 100.0(1), P-C1-C2 127.7(1), C1-C2-C3 120.9(2) C2-C3-C4 122.5(2), C3-C4-C5 125.1(1), P-C5-C4 123.4(1); torsional angles: C1-P-C5-C4 2.0(2), P-C1-C2-C3 0.3(3), C5-P-C1-C2 1.2(2), C1-C2-C3-C4 -5.2(3), C2-C3-C4-C5 8.8 (3), C3-C4-C5-P -7.0(3).

In contrast to vinylcarbene complexes synthetically useful yields may be obtained from fused arylcarbene complexes. The phosphaannulation of the 1-naphthylcarbene ligand in **4a,b** affords a >70% yield of the phosphaphenanthrene hydroquinone complexes **5a,b**, partly along with a small amount of decomplexation product **6** (eq. 2). The incorporation of the phosphaalkyne is highly regioselective: The sterically less shielded terminus of the triple bond system is connected exclusively with the carbene carbon atom, while the bulky *tert.* butyl substituent ends up next to the phenolic group. A corresponding regiochemical preference is known from benzannulation reactions with alkynes[30] In addition to NMR data the regiochemistry and the coordination of the phosphinine ring have been confirmed by an X-ray analysis of **5a** (fig. 2). Ring-puckering which continues

in the adjacent arene ring and alternating bond lengths within the phosphorous heterocycle resemble those encountered in the phosphinine ligand of **3**; the conformation of the $Cr(CO)_3$-unit differs in such a way that one carbonyl group is nearly eclipsed with respect to the phosphorous atom. A similar conformation which obviously minimizes steric interactions between the ring substituents and the carbonyl ligands has been observed for $Cr(CO)_3$ complexes of phenanthrene[31] and 1-4-tetra-substituted naphthols[32].



4a : R=Me
4b : R=Et

2

5a : R=Me
5b : R=Et

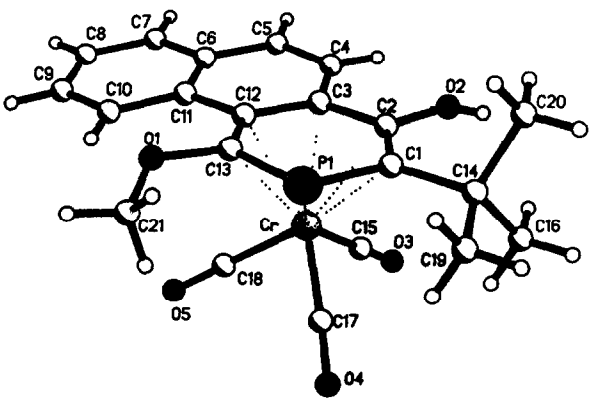
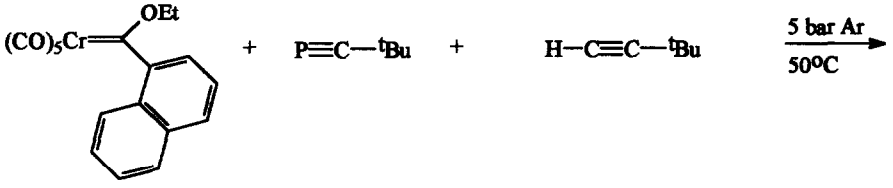
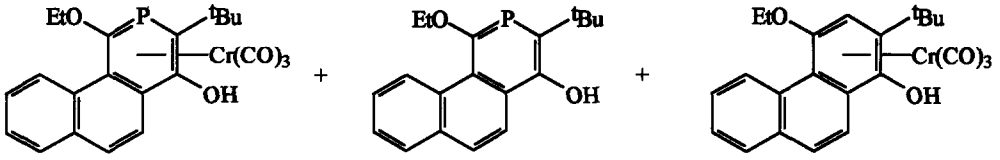


Fig. 2. Molecular structure of **5a**. Selected bond lengths (Å) and angles (°): Cr-P1 2.4591(4), $Cr\text{-}C_{heterocycle}$ 2.290(1) (average), $Cr\text{-}C_{carbonyl}$ 1.836(2) (average), C1-P1 1.768(1) C13-P1 1.759(1), C1-C2 1.400(2) C2-C3 1.438(2), C3-C12 1.428(2), C12-C13 1.437(2), C1-P1-C13 101.73(6), P1-C1-C2 121.4(1), C1-C2-C3 126.4(1), C2-C3-C12 124.0(1), C3-C12-C13 117.9(1), P1-C13-C12 128.2(1); torsional angles. C1-C2-C3-C12 0.3(4), C2-C3-C12-C13 4.8(4), C3-C12-C13-P1 -4 2(4), C12-C13-P1-C1 -0 5(3), C13-P1-C1-C2 5.2(2), P1-C1-C2-C3 -5.8(4).

In order to estimate the relative rates of carbene annulation by alkynes and phosphaalkynes a competition experiment was carried out comparing phosphaalkyne **2** and *tert.*butyl acetylene which have similar steric requirements. Based on quantitative analysis of the annulation products **5b, 6b** and **7** by NMR the phosphaalkyne reacts about 6 times as fast as the alkyne when in equimolar amounts exposed to a ^tBuOMe solution of naphthylcarbene complex **4b** which is warmed to 50°C under 5 bar argon (eq. 3)

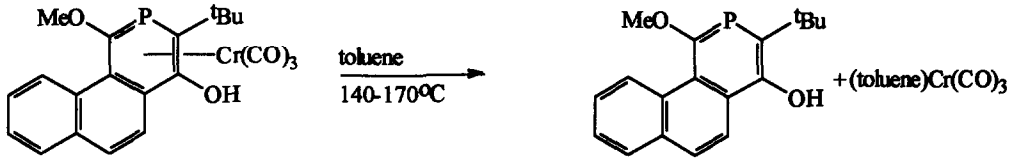


4b **2** (eq.3)

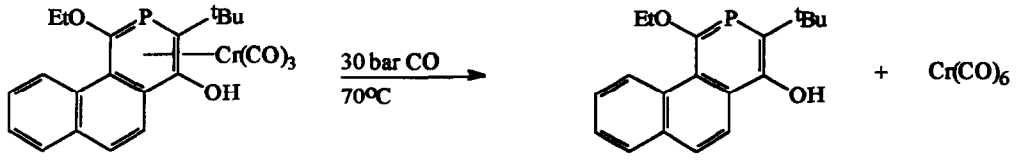


5b **6b** **7**

The coordination of the phosphinine ring to the $Cr(CO)_3$-fragment in the phosphaannulation product is rather strong. When **5a** is warmed in toluene, slow decomplexation occurs no sooner than at 140°C leading to the free phosphahydroquinone **6a** while the metal is trapped as (toluene)$Cr(CO)_3$. No haptotropic metal migration to the terminal arene ring is observed under these conditions. As precedented in the (arene)$Cr(CO)_3$ series much milder conditions are sufficient for decomplexation when carried out under CO pressure. For instance, warming of an ether solution of **5b** to 70°C under 30 bar CO results in a 95% yield of uncoordinated phosphahydroquinone **6b** (eq. 4).



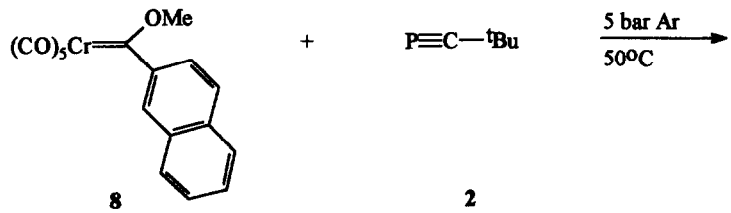
5a **6a** (eq.4)



5b **6b**

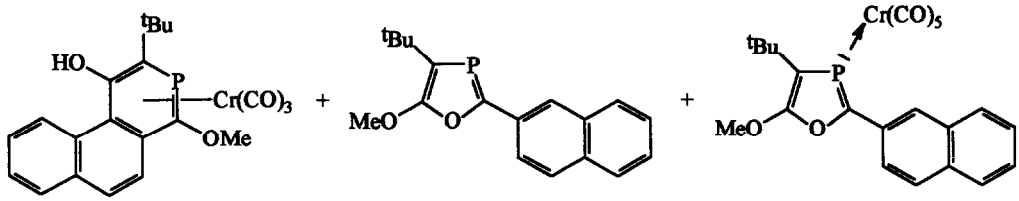
COMPETITIVE PHOSPHAARENE AND OXAPHOSPHOLE FORMATION

Reactions of chromium alkoxy(aryl)carbene complexes with non-nucleophilic alkynes are known to give rise to various types of cycloaddition products with six-membered oxygenated arenes generally prevailing[4a,d]. The chemoselectivity is influenced by the substitution pattern both in the carbene ligand and in the alkyne, for instance, steric congestion in the alkyne favours the formation of cyclobutenones[33] whereas bulky or *ortho*-disubstituted aryl substituents in the carbene ligand may lead to furans[34] or indenes[35]. In the phosphaannulation, the substitution pattern in the carbene ligand has even a more pronounced effect on the chemoselectivity Changing the 1-naphthyl group in complex **4a** to a 2-naphthyl substituent in **8** the yield of phosphaphenanthrene annulation product **9** drops from 82% to 19% while a five-membered cycloaddition product, the oxaphosphole **10** and its $Cr(CO)_5$ adduct **11**, is isolated in a similar amount (eq. 5) Analogous to benzannulation reactions with alkynes[36] no linear annulation product (phosphaanthracene) was detected.



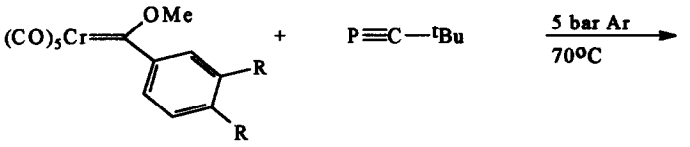
8 **2**

(eq.5)



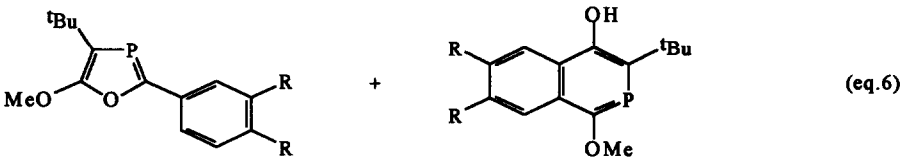
9 **10** **11**

The competition of phosphaannulation and oxaphosphole formation is a general feature of reactions of alkoxy(aryl)carbene complexes and phosphaalkyne **2**. Using molecular sieve (3Å) as CO absorber the phenylcarbene complex **12** affords oxaphosphole **13** along with two minor products which could not be separated by chromatography; NMR spectroscopic analysis indicated that one component of this mixture is the 3-phosphanaphthalene **14** while the other - a $Cr(CO)_5$ coordinated organophosphorus compound - could not be fully identified. Introduction of donor substituents such as methoxy groups into the arene ring shifts the product distribution to the five-membered cycloaddition product Upon reaction of complex **15** containing a non-chelating 1,2-dimethoxy substitution pattern with phosphaalkyne **2** the oxaphosphole **16** and the phosphaarene **17** are obtained in an appproximately 2/1 ratio (eq 6).



12 : R=H
15 : R=OMe

2

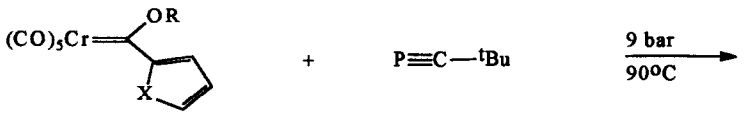


(eq.6)

13 R=H
16 R=OMe

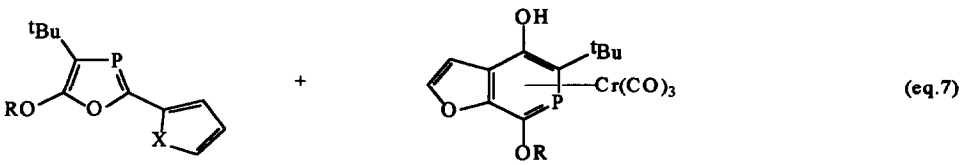
14 · R=H
17 R=OMe

The competition of phosphaannulation and oxaphosphole formation seems to be a balance of steric and electronic factors. Whereas the chemoselectivity observed in the 1- and 2-naphthylcarbene series might be traced back mainly to steric factors, the results obtained from phenylcarbene complexes could be rationalized in terms of electronic control. Further support for electronic control comes from reactions involving five-membered heteroaromatic carbene ligands: Using the 2-furylcarbene complex **18** the phosphaannulation prevails by 2/1 **(20/19)**, while with the 2-thienyl analogue **21** the oxaphosphole formation dominates by 10/1 **(22/23)** (eq 7)



18 X=O , R=Me
21 . X=S , R=Et

2

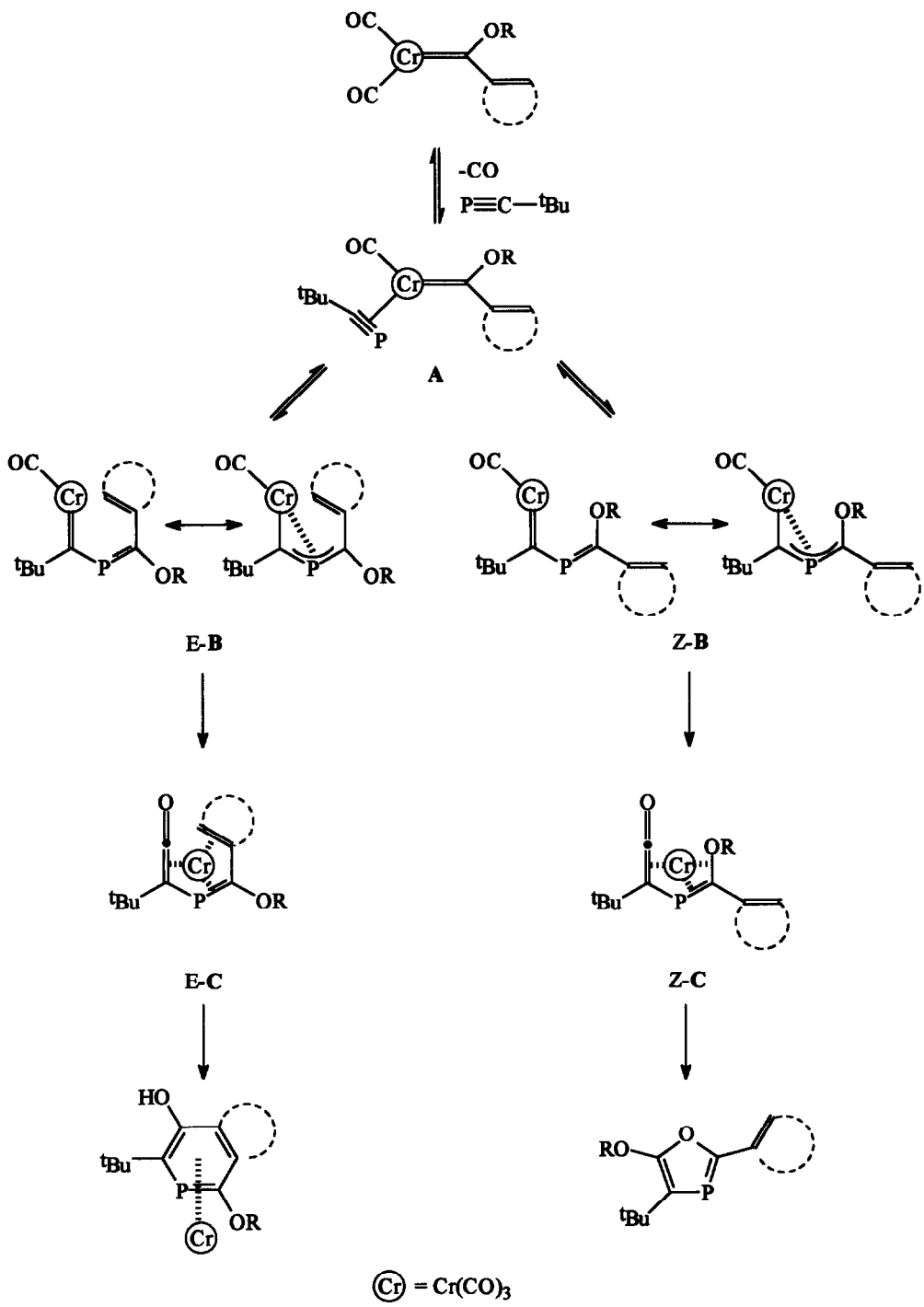


(eq.7)

19 : X=O , R=Me
22 : X=S , R=Et

20 · X=O , R=Me ,Y= –
23 : X=S , R=Et , Y=Cr(CO)3

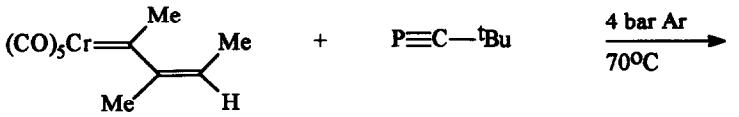
A mechanistic description of the competing phosphaannulation and oxaphosphole formation starts from a common carbene-phosphaalkyne-complex intermediate **A**. Insertion of the phosphaalkyne into the metal-carbene bond may lead either to an *E*- or a *Z*-isomer **B** which can be described as a σ,π-phosphaallyl or a π-phosphaalkenylcarbene complex[37]. The *E*-isomer is expected to undergo a carbene-CO coupling to give *E*-vinyl ketene **C** which by an electrocyclic 1,6-ring closure is converted to the annulation product. The *Z*-vinyl ketene **C**, however, obviously undergoes an overall alkoxy shift to the ketene carbonyl carbon atom followed by a cyclization to give the oxaphosphole skeleton (scheme 1).



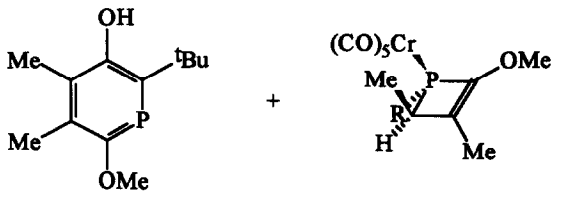
Scheme 1 Mechanistic scheme for the competition of phosphaannulation and oxaphospole formation.

The competition of carbene annulation and formation of five-membered heterocycles has precedents in the reaction of carbene complexes with alkynes. Whereas chromium-coordinated alkoxy(aryl)- and alkoxy(vinyl)carbene ligands are generally incorporated into hydroquinones, the furan skeleton was obtained as the major product from the bulky ferrocenyl(methoxy)carbene complex upon reaction with tolane[34a]. The connectivity of alkyne, carbene and carbonyl ligands leading to the furan nucleus was established by labelling studies[34b]. Extension of this work to the formation of the oxaphosphole ring implies that the phosphorous atom is attached to the former carbene carbon and the alkoxy substituent has migrated to the former carbonyl carbon atom.

Further support for the idea that similar steps in the mechanism are operative in the reaction of carbene complexes with alkynes and phosphaalkynes is provided from the reaction of *Z*-2-butenylcarbene complex **1b** with phosphaalkyne **2**. The *Z*-isomer was chosen in order to hamper the final heterocyclic ring closure, and thus eventually to trap suggested phosphavinylcarbene or ketene intermediates. In analogy to the reaction of the *E*-isomer **1a** again the phosphinine complex **3** was observed as a minor product indicating that partial isomerization across the C=C bond must have occurred in the course of the reaction[38]. In addition, an orange solid was isolated in low yield; by NMR and IR spectroscopy its structure was elucidated as dihydrophosphete complex **24**, the intramolecular [2+2] cycloaddition product of a presumed phosphadienylketene intermediate C (eq. 8)[39]. NMR-Data suggest that a single diastereomer was obtained. The $^3J_{P,H}$ coupling constant (16.1 Hz) observed for the 2-methyl group is consistent with a *cis*-configuration with respect to the metal carbonyl fragment[40]



1b **2**

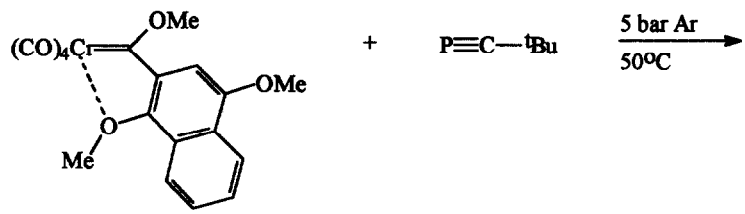


(eq.8)

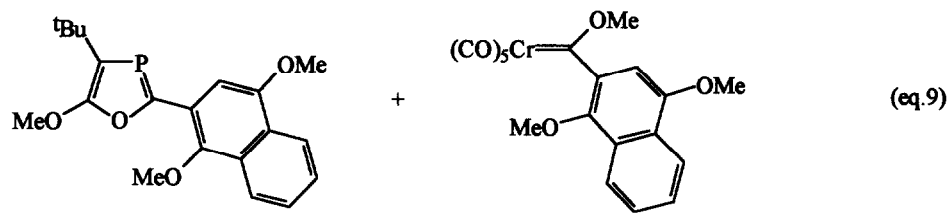
3 **24**

CARBENE CHELATE COMPLEXES IN CYCLOADDITION REACTIONS

In arylcarbene complexes *ortho*-methoxy substitutents have been used to control the regiochemistry of carbene annulation by *alkynes*. By this strategy, annulation of 2-naphthylcarbene ligands could be shifted from the generally preferred phenanthrene formation to the construction of the anthracene skeleton[17a]. An extension of this work to the *phosphaalkyne* demonstrated that - in this case - the phosphaannulation could not successfully compete with oxaphosphole formation. No linear phosphaanthracene complex could be detected after the carbene chelate complex **25** was reacted with phosphaalkyne **2**. Only oxaphosphole **26** was observed along with the carbonylation product **27** (eq. 9). Since separation by chromatography turned out to be tedious the carbene complex was modified into the easily separable aminocarbene analogue **28**.

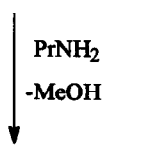


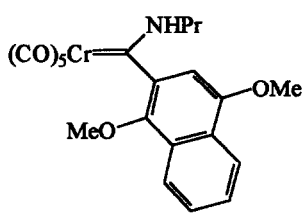
25 **2**



(eq.9)

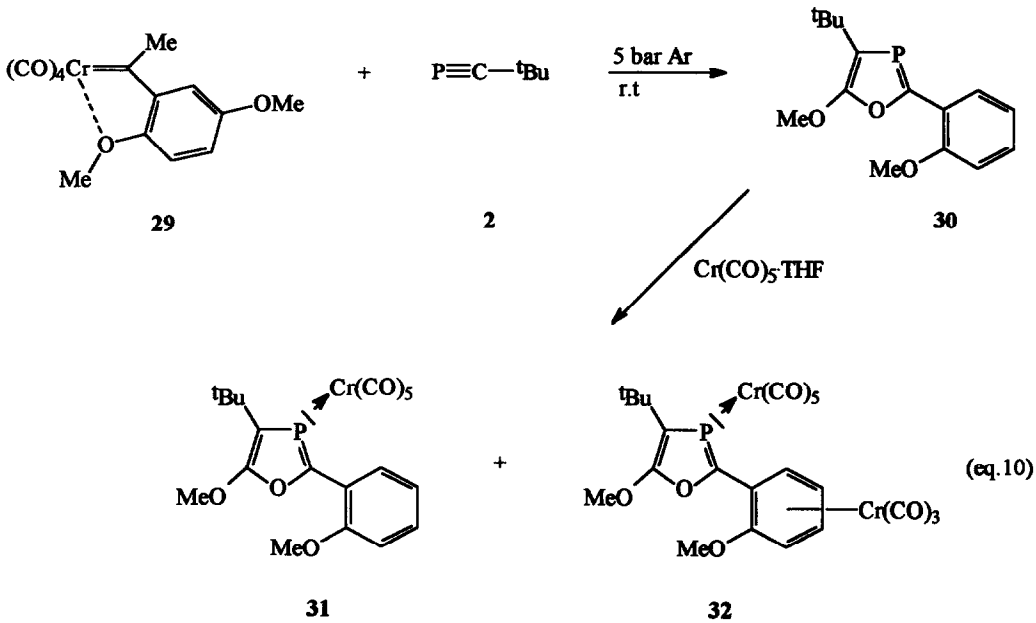
26 **27**





28

A clean cycloaddition to give the five-membered phosphorous heterocycle occurs with the *ortho*-anisylcarbene chelate **29** (eq. 10). Since carbene chelates often allow milder conditions than their non-chelated analogues we tried to identify possible intermediates. However, at temperatures as low as -30° the oxaphosphole **30** was the only isolable product. A similar result was obtained from UV-irradiation under these conditions; no detectable amount of phosphaannulation product was observed indicating that *E/Z*-isomerization either in the presumed phosphaalkenylcarbene or phosphavinyl ketene intermediates is slow compared with carbonylation or ring-closure (scheme 1).

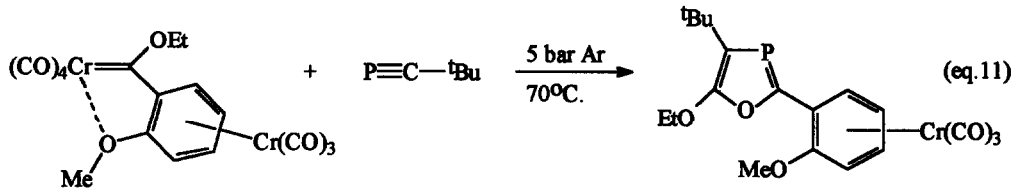


29 **2** **30**

31 **32**

(eq.10)

While synthetic routes to aza- and thiaphospholes have been recently reported[41] and structural information on the thiaphosphole skeleton is available[42], only benzannulated derivatives of 1,3-oxaphospholes have been known[43]. Efforts to obtain crystals of **30** suitable for X-ray diffraction by coordination of the phosphorous atom to the $Cr(CO)_5$ fragment resulted in a mixture of phosphine and arene complexes **31** and **32**. A clean and high-yield access to coordinated oxaphospholes, however, is provided by the reaction of the chromium-coordinated carbene chelate **33** with phosphaalkyne **2** (eq 11). Complex **34** contains a planar five-membered ring with two distinctly different phosphorous-carbon bond lengths, 1.705(4) and 1.772(4) Å, indicative for a P=C and a P-C bond. The $Cr(CO)_3$ fragment is coordinated unsymmetrically to the anisyl group and is shifted away from the substituted ring carbon atoms adopting a nearly eclipsed conformation as expected for donor-substituted arene ligands (fig. 3).



33 **2** **34**

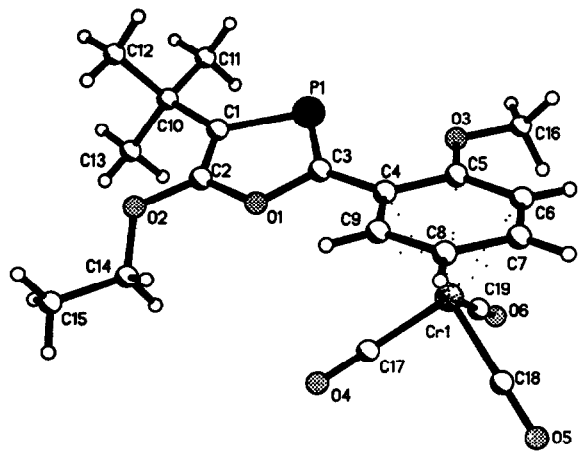


Fig. 3. Molecular structure of **34**. Selected bond lengths (Å) and angles (°): C1-P1 1.772(4), P1-C3 1 705(4), C3-O1 1.369(5), O1-C2 1 355(6), C2-C1 1.339(7), C2-O2 1.339(6), Cr-C_{anisyl} 2.233(4) (average), Cr-$C_{carbonyl}$ 1.834(5) (average): C1-P1-C3 89.5(2), P1-C3-O1 113.6(3), C3-O1-C2 110.8(3), O1-C2-C1 116.9(4), C2-C1 116.9(4), C2-C1-P1 109.2(3); torsion angles (°) C1-P1-C3-O1 0 4(7), P1-C3-O1-C2 0.0(1), C3-O1-C2-C1 -1.0(5), O1-C2-C1-P1 1.3(4), C2-C1-P1-C3 -0.9(3), P1-C3-C4-C5 -15.5(6), O1-C3-C4-C9 -14.7(5).

CONCLUSION

The P≡C triple bond in kinetically stabilized phosphaalkynes can be included into the diversity of Fischer-type metal carbene/alkyne reactions providing access to highly substituted phosphahydroquinones and 1,3-oxaphospholes. The chemoselectivity which may be controlled by the substitution pattern in the carbene ligand, the regioselectivity of both carbene annulation and cycloaddition and the variety of available carbene complexes offer a promising basis for novel synthetic routes to polyfunctionalized phosphorous heterocycles.

EXPERIMENTAL

General technique

All reactions and workup operations were carried out under an atmosphere of dried inert gas (Ar or N_2). Solvents were dried using standard methods, distilled, N_2-saturated and stored under N_2. Silica gel used for chromatography (E. Merck, type 60, 0.063 - 0.2 mm) was dried at high vacuum and kept under N_2. The following instruments served for spectroscopic characterization. IR-spectra: Perkin Elmer 281 and Bruker IFS 88; NMR-spectra: Bruker AC 300, Bruker WH 400; mass spectra: Varian MAT CH 7A and Varian MAT 711 NMR data are reported in ppm using TMS as internal standard (^1H, ^{13}C) or 85% - H_3PO_4 as external standard (^{31}P).

Tricarbonyl(5,6-dimethyl-1-hydroxy-4-methoxy-2-tert.butyl-3-phosphinine)chromium (3). 0.6 g (2.07 mmol) Pentacarbonyl[*E*-2-butenyl(methoxy)carbene]chromium (**1a**)[44] and 0.23 g (2.30 mmol) 2,2-dimethylpropylidynephosphane (**2**)[28] were dissolved in 20 ml *tert.*BuOMe. The solution was exposed to a pressure of 4 bar Ar and then warmed to 100° for 2 hr Removal of the solvent and chromatography on silica gel at -25° using dichloromethane/petroleum ether as eluent afforded a marginal amount of yellow crystals. Single crystals suitable for X-ray analysis were obtained by recrystallization from dichloromethane/petroleum ether (1/3) MS *m/z*: 362 ($C_{15}H_{19}CrO_5P$ 362.3)

Tricarbonyl[1-4,4a:10a-η^6-1-hydroxy-4-methoxy-2-tert.butyl-3-phosphaphenanthrene]chromium (5a) and ***1-hydroxy-4-methoxy-2-tert.butyl-3-phosphaphenanthrene (6).*** A solution of 2.72 g (7.50 mmol) pentacarbonyl[methoxy(1-naphthyl)carbene]chromium (**4a**)[36] and 0.75 g (7.50 mmol) phosphaalkyne 2 in 20 ml *tert.*BuOMe was warmed to 50° for 2 hr unter 5 bar Ar. The solvent was removed and the residue was purified by chromatography on silica gel at -25° using dichloromethane/petroleum ether (1/3 to 1/0) as eluent First, a yellow powder of **6a** was obtained which was recrystallized from dichloromethane/petroleum ether (1/5) From the second band dark red crystals of **5a** were isolated after recrystallization from dichloromethane/petroleum ether (1/1). **5a:** 2.59 g (82%) IR (KBr, ν_{OH} cm^{-1}): 3577, (C_6H_{14}, ν_{CO} cm^{-1}): 1965s, 1885s,br. ^1H-NMR (CD_3COCD_3, 400 MHz): δ 1.57 (d, 9H, $C(CH_3)_3$; $^4J_{P,H}$= 2.75 Hz); 4.00 (d, 3H, OCH_3, $^4J_{P,H}$= 3.04 Hz), 7.64 (m, 2H, H-6, H-7; $^3J_{H,H}$= 7.12, $^4J_{H,H}$= 1.40 and 1 73 Hz); 7.85 (d, 1H, H-9; $^3J_{H,H}$= 9 59 Hz), 7 89 (dd, 1H, $^3J_{H,H}$= 7.54 Hz); 8 32 (d. 1H, H-10; $^3J_{H,H}$= 9.59 Hz); 8 55 (s, 1H, OH); 9.35 (dd, 1H, H-5; $^3J_{H,H}$= 8.09 Hz, $^4J_{H,H}$= 1 28 Hz). ^{13}C-NMR (CD_3COCD_3, 100.4 MHz): δ 31.62 (d, $C(CH_3)_3$, $^3J_{P,C}$= 14 15 Hz), 38.01 (d, $C(CH_3)_3$, $^2J_{P,C}$= 19 55 Hz), 59.93 (d, OCH_3; $^3J_{P,C}$= 34.33 Hz), 101 06 (d, C-4a, $^2J_{P,C}$= 7.65 Hz), 114 73 (d, C-2; $^1J_{P,C}$= 60 07 Hz); 96.97 (s), 123.27 (s), 128.71 (s), 129.19 (s), 129 39 (s), 130.07 (s), 131 04 (s), 131.12 (s), 133.65 (s) (C-4b-C-10a); 134 04 (d, C-1; $^2J_{P,C}$= 7 55 Hz); 154 72 (d, C-4, $^1J_{P,C}$= 68.02 Hz), 233.49 (s, $Cr(CO)_3$) ^{31}P-NMR (CD_3COCD_3, 121.5 MHz) δ -26.50 MS *m/z* (%): 434 (Found C, 57 86; H, 4 43%; $C_{21}H_{19}CrO_5P$ 434.3 Requires C, 58.07, H, 4.41%) **6a** 0.15 g (7%) IR (KBr, ν_{OH} cm^{-1}): 3550. ^1H-NMR (CD_3COCD_3, 400 MHz): δ 1.68 (d, 9H, $C(CH_3)_3$; $^4J_{P,H}$= 2 49 Hz), 4.29 (d, 3H, OCH_3; $^4J_{P,H}$= 2 97 Hz); 7.61 (ddd, 2H, H-6, H-7; $^3J_{H,H}$= 7 22 Hz); 7.92 (ddd, 2H, H-8, H-9, $^3J_{H,H}$= 8.32 Hz, $^4J_{H,H}$= 2 38 Hz); 8.39 (d, 1H, H-10, $^3J_{H,H}$= 9.27 Hz), 8 01 (s, 1H, OH), 9 68 (dd, 1H, H-5; $^3J_{H,H}$= 7 27 Hz) ^{13}C-NMR (CD_3COCD_3, 100.4 MHz) δ 31 64 (d, $C(CH_3)_3$; $^3J_{P,C}$= 15 55 Hz), 38 97 (d, $C(CH_3)_3$; $^2J_{P,C}$= 23.69 Hz); 59 07 (d, OCH_3; $^3J_{P,C}$= 38.33 Hz); 131 36 (d, C-4a, $^2J_{P,C}$= 6.94 Hz), 122 931 (s), 122 933 (s), 127 42 (s), 127.52 (s), 128 47 (s), 129.30 (s), 129 38 (s), 130 52 (s), 133 69 (s) (C-4b-C-10a); 149 87 (d, C-1, $^2J_{P,C}$= 11.85 Hz), 153 77 (d, C-2; $^1J_{P,C}$= 47.17 Hz), 189.80 (d, C-4, $^1J_{P,C}$ = 46 04 Hz). ^{31}P-NMR (CD_3COOD_3, 121.5 MHz) δ 124 30 MS *m/z*: 298 ($C_{18}H_{19}O_2P$ 298 3)

Tricarbonyl(1-4,4a:10a-η^6-1-hydroxy-4-ethoxy-2-tert.butyl-3-phosphaphenanthrene)chromium (5b). A solution of 2.82 g (7.50 mmol) pentacarbonyl[ethoxy(1-naphthyl)carbene]chromium (**4b**)[36] and 0.75 g (7.50 mmol) phosphaalkyne **2** in 20 ml *tert.*BuOMe was warmed to 50° for 2 hr under 5 bar Ar. Workup as described for the preparation of **5a** gave red crystals of **5b**. **5b**: 2.41 g (72%). IR (KBr, ν_{OH} cm^{-1}) 3587,

(C_6H_{14}, ν_{CO} cm^{-1}): 1957 s, 1887 s,br ^{1}H-NMR (CD_3COCD_3, 400 MHz): δ 1.57 (d, 9H, C(CH_3), $^4J_{P,H}$= 2 09 Hz), 1.58 (t, 3H, OCH_2CH_3; $^3J_{H,H}$= 6.87 Hz); 4.09 (dq, 1H; $^2J_{H,H}$= 14 28 Hz, $^3J_{H,H}$= 7.14 Hz); 4.30 (dq, 1H; $^2J_{H,H}$= 14.30 Hz, $^3J_{H,H}$= 7 15 Hz), (OCH_2); 7.66 (m, 2H, H-6, H-7, $^3J_{H,H}$= 7.70 Hz); 7 90 (m, 4H, H-8-H-10, OH; $^3J_{H,H}$= 9.22 Hz); 9.50 (d, 1H, H-5; $^3J_{H,H}$= 8 30 Hz) ^{13}C-NMR (CD_3COCD_3, 100.4 MHz). δ 15.20 (d, CH_3CH_2O, $^4J_{P,C}$= 3.99 Hz); 31.46 (d, C(CH_3)$_3$; $^3J_{P,C}$= 14.25 Hz); 38.03 (d, C(CH_3)$_3$; $^2J_{P,C}$= 19.43 Hz); 70.15 (d, CH_3CH_2O; $^2J_{P,C}$= 35.25 Hz); 100.89 (d, C-4a; $^2J_{P,C}$= 7.64 Hz); 115.2 (d, C-2; $^1J_{P,C}$= 60.36 Hz); 97.04 (s), 123.34 (s), 128.60 (s), 129 17 (s), 129 41 (s), 130.17 (s), 131 09 (s), 131.11 (s), 133.70 (s) (C-4b-C-10a); 133.90 (d, C-1; $^2J_{P,C}$= 7.55 Hz); 153.72 (d, C-4; $^1J_{P,C}$= 68.21 Hz); 233.67 (s, Cr(CO)$_3$). ^{31}P-NMR (CD_3COCD_3, 121.5 MHz): δ -24.70. MS *m/z*: 448. ($C_{22}H_{21}CrO_5P$ 448.4).

Competition of phosphaalkyne 2 and tert.butyl acetylene for carbene annulation. A solution of 1.42 g (3.77 mmol) pentacarbonyl[ethoxy(1-naphthyl)carbene]chromium (**4b**)[36], 0.38 g (3 77 mmol) phosphaalkyne **2** and 0.31 g (3 77 mmol) *tert.*butyl acetylene in 20 ml diethylether containing 5 g molecular sieve (3Å) was warmed to 60° for 2 hr under 5 bar Ar. After removal of the solvent the residue is dissolved in CD_3COCD_3. ^{1}H-NMR spectroscopic analysis indicated a product distribution of **5b/6b/7** = 27/3/5.

Decomplexation experiments

Thermal decomplexation. A toluene solution of 0.19 g (0.44 mmol) **5a** was warmed in an autoclave to 170° for 2 hr After removal of the solvent the residue was analyzed by ^{1}H- and ^{13}C-NMR spectrocopy which indicated an essentially quantitative formation of **6a** and (toluene) Cr(CO)$_3$

Ligand exchange A solution of 0.90 g (2 mmol) **5b** in 40 ml diethylether was warmed in an autoclave to 70°C for 14 hr under 30 bar CO. Then the solvent and $Cr(CO)_6$ were removed at 30° in vacuo. Chromatography of the residue on silica gel at 10° using ether/petroleum ether and recrystallization afforded yellow crystals. **6b** 0 63 g (95%). ^{1}H-NMR (CD_3COCD_3, 400 MHz). δ 1.67 (d, 9H, C(CH_3)$_3$; $^4J_{P,H}$= 2.45 Hz); 1.71 (t, 3H, CH_3CH_2O; $^3J_{H,H}$= 6 29 Hz), 4 88 (q, 2H, CH_3CH_2O; $^3J_{H,H}$= 6 74 Hz); 7 61 (m, 2H, H-6, H-7, $^3J_{H,H}$= 7 80 Hz); 7.88 (d, 3H, H-8, H-9, OH; $^3J_{H,H}$= 9 63 Hz); 8.39 (d, 1H, H-10; $^3J_{H,H}$= 9.32 Hz); 9.80 (d, 1H, H-5, $^3J_{H,H}$= 7 30 Hz). ^{13}C-NMR (CD_3COCD_3, 100 4 MHz). δ 15.39 (d, CH_3CH_2O; $^4J_{P,C}$= 4.08 Hz); 31 64 (d, C(CH_3)$_3$; $^3J_{P,C}$= 15.46 Hz); 38.94 (d, C(CH_3)$_3$; $^2J_{P,C}$= 23.67 Hz); 68.61 (d, CH_3CH_2O; $^2J_{P,C}$= 39.32 Hz); 129.43 (d, C-4a; $^2J_{P,C}$= 5.28 Hz); 122.92 (s), 122.99 (s), 127 29 (s), 127.46 (s), 128.43 (s), 129.16 (s), 129 23 (s), 130.57 (s), 133.70 (s) (C-4b-C-10a); 149.71 (d, C-1; $^2J_{P,C}$= 11 85 Hz); 153.97 (d, C-2; $^1J_{P,C}$= 47.47 Hz); 188.74 (d, C-4, $^1J_{P,C}$= 46.56 Hz). ^{31}P-NMR (CD_3COCD_3, 121.5 MHz): δ 125 80 MS *m/z*: 312 ($C_{19}H_{21}O_2P$ 312 4).

Tricarbonyl(1-4, 4a: 10a-η^6-4-hydroxy-1-methoxy-3-tert.butyl-2-phosphaphenanthrene)chromium (9), 2-naphthyl-5-methoxy-4-tert.butyl-1,3-oxaphosphole (10) and pentacarbonyl(2-naphthyl-5-methoxy-4-tert.butyl-1,3-oxaphosphole)chromium (11). A solution of 1.55 g (4.28 mmol) pentacarbonyl-[methoxy(2-naphthyl)carbene]chromium (**8**)[36] and 0.60 g (6.00 mmol) phosphaalkyne **2** in 25 ml ^{t}BuOMe was warmed to 50° for 5 hr under 4 bar Ar. The solvent was removed, and chromatography of the residue on silica gel at -25° using dichloromethane/petroleum ether (1/3 to 1/1) as eluent afforded first a mixture of **10/11** and then a red band containing the phosphaarene complex **9** which was isolated as red crystals after recrystallization from dichloromethane/petroleum ether (2/5). Further chromatography of the oxaphosphole mixture on silica gel with ether/petroleum ether (1/15) and recrystallization of the products from dichloromethane/petroleum ether (1/10) gave a dark red powder of **10** and an orange solid of **11.** **9** 0.35 g (19%) IR (CH_2Cl_2, ν_{CO} cm^{-1}) 1960 s, 1890 s. ^{1}H-NMR (CD_3COCD_3, 300.1 MHz). δ 1.53 (d, 9H, C(CH_3)$_3$); 3 93 (d, 3H, OCH_3); 7 65 (m, 6H, H-6-H-10, OH), 9 35 (d, 1H, H-5; $^3J_{H,H}$= 7 86 Hz). ^{13}C-NMR (CD_3COCD_3, 75 5 MHz) δ 31.50 (d, C(CH_3); $^3J_{P,C}$= 14.41 Hz); 38.35 (d, C(CH_3)$_3$, $^2J_{P,C}$= 19.82 Hz), 59.41 (d, OCH_3; $^3J_{P,C}$= 32.18 Hz); 105 89 (d, C-10a; $^2J_{P,C}$= 6.34 Hz); 110.35 (d, C-3; $^1J_{P,C}$= 60 60 Hz), 90 82 (s), 119.78 (s), 128.38 (s), 128.62 (s), 128.90 (s), 129.76(s), 131.99 (s), 132 09 (s), 132 99 (s) (C-4a-C-10), 140.71 (d, C-4; $^2J_{P,C}$= 8 53 Hz); 150 51 (d, C-1; $^1J_{P,C}$= 63 40 Hz); 233.77 (s, Cr(CO)$_3$). ^{31}P-NMR ($CDCl_3$, 121 5 MHz): δ -33 34. MS *m/z*: 434. (Found: C, 57.41; H, 4.61%; $C_{21}H_{19}CrO_5P$ 434.3. Requires C, 58.07; H, 4 41%) **10** 0 12 g (9%). ^{1}H-NMR ($CDCl_3$, 300.1 MHz) δ 1.35 (d, 9H, C(CH_3)$_3$; $^4J_{P,H}$= 1.29 Hz); 4 10 (s, 3H, OCH_3), 7 43 (m, 2H, H-6', H-7'; $^3J_{H,H}$= 7 08 Hz); 7 76 (dd, 2H, H-3', H-4',

$^3J_{H,H}$= 9 14 Hz), 7.80 (dd, 2H, H-5', H-8'; $^3J_{H,H}$= 8.20 Hz, $^4J_{H,H}$= 1.61 Hz); 8.06 (s, 1H, H-1'). ^{13}C-NMR ($CDCl_3$, 75.5 MHz)· δ 31 37 (d, C(CH_3)$_3$; $^3J_{P,C}$= 7.77 Hz); 31.59 (d, C(CH_3)$_3$; $^2J_{P,C}$= 14.79 Hz); 58.44 (s, OCH_3); 121.18 (d, C-4; $^1J_{P,C}$= 44.22 Hz); 119 47 (d), 121 69 (d), 125.76 (d), 126.55, 127 76, 128.20 (d), 128.32, 132.23 (d), 132 89, 133 54 (C-1'-C-8a'); 159.07 (d, C-5; $^2J_{P,C}$= 5.36 Hz), 180.07 (d, C-2; $^1J_{P,C}$= 47.24 Hz). ^{31}P-NMR ($CDCl_3$, 121.5 MHz): δ 121.05. MS *m/z:* 298. ($C_{18}H_{19}O_2P$ 298 3). **11**: 0 16 g (8%). IR (C_6H_{14}, ν_{CO} cm^{-1}). 2070 m, 1961s, 1952s,sh. ^{1}H-NMR ($CDCl_3$, 300 1 MHz): δ 1.45 (d, 9H, C(CH_3)$_3$; $^4J_{P,H}$= 0.95 Hz); 4.10 (s, 3H, OCH_3); 7.48 (m, 2H, H-6', H-7'; $^3J_{H,H}$= 6.30 Hz); 7.83 (d, 1H; $^3J_{H,H}$= 9 37 Hz), 7.85 (d, 1H) (H-3', H-4'); 7 72 (ddd, 1H, $^3J_{H,H}$= 8.43 Hz, $^4J_{H,H}$= 1 51 Hz), 7.88 (d, 1H; $^3J_{H,H}$= 8.05 Hz) (H-5', H-8'); 8.17 (s, 1H, H-1'). ^{13}C-NMR ($CDCl_3$, 75.5 MHz). δ 31.51 (d, C(CH_3)$_3$; $^3J_{P,C}$= 4.91 Hz), 32.40 (d, C(CH_3)$_3$; $^2J_{P,C}$= 10.94 Hz); 58.02 (s, OCH_3); 123.49 (d, C-4; $^1J_{P,C}$= 8.38 Hz); 118.49 (s), 125 30 (d), 126.69 (s), 127 71 (s), 128.20 (s), 128.41 (s), 130.02 (d), 133.06 (d), 133.09 (d) (C-1'-C-8a'), 161 12 (d, C-5; $^2J_{P,C}$= 2.26 Hz); 179.88 (d, C-2; $^1J_{P,C}$= 23.32 Hz); 214.82 (d, cis-CO; $^2J_{P,C}$= 14.49 Hz); 220.83 (d, trans-CO; $^2J_{P,C}$= 4.08 Hz). ^{31}P-NMR ($CDCl_3$, 121.5 MHz)· δ 130.35. MS *m/z:* 490. ($C_{23}H_{19}CrO_7P$ 490.4).

2-Phenyl-5-methoxy-4-tert.butyl-1,3-oxaphosphole (13) and 4-methoxy-2-tert.butyl-3-phosphanaphthol-1 (14). A solution of 0.58 g (1 86 mmol) pentacarbonyl[methoxy(phenyl)carbene]chromium (**12**)[45] and 0.22 g (2 20 mmol) phosphaalkyne **2** in 20 ml DME was warmed to 80° for 5 hr in the presence of molecular sieve (3Å) under 5 bar Ar The solvent was removed in vacuo, and the residue was worked up by chromatography on silica gel. Elution at -25° with dichloromethane/petroleum ether (1/3) afforded a brown oil **13** and a mixture containing **14** and another unidentified product **13**. 0.16 g (35%). ^{1}H-NMR ($CDCl_3$, 300.1 MHz) δ 1.33 (d, 9, C(CH_3)$_3$), 4.03 (s, 3H, OCH_3), 7 22 (dd, 1H, H-4', $^3J_{H,H}$= 7 50 Hz, $^4J_{H,H}$= 1.03 Hz); 7.31 (dd, 2H, H-3', H-5'; $^3J_{H,H}$= 7.65 Hz), 7.68 (dd, 2H, H-2', H-6'; $^3J_{H,H}$= 7 60 Hz, $^4J_{H,H}$= 1.70 Hz). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 31.38 (d, C(CH_3)$_3$; $^3J_{P,C}$= 7.82 Hz); 58.31 (s, OCH_3); 120.96 (d, C-4; $^1J_{P,C}$= 44.07 Hz); 122.29 (d), 127.52 (d), 128.63 (d), 134.86 (d) (C-1'-C-6'); 158 80 (d, C-5; $^2J_{P,C}$= 5.43 Hz); 180 81 (d, C-2, $^1J_{P,C}$= 47 02 Hz) ^{31}P-NMR ($CDCl_3$, 121 5 MHz): δ 118.05. MS *m/z* 248. ($C_{14}H_{17}O_2P$ 248 3). **14**: 0 02 g (6%). ^{1}H-NMR ($CDCl_3$, 300.1 MHz) δ 1.66 (d, 9H, C(CH_3)$_3$; $^4J_{P,H}$= 2.42 Hz); 4.21 (d, 3H, OCH_3; $^4J_{P,H}$= 2.87 Hz); 7 57 (m, 2H, H-6, H-7), 8.30 (d, 2H, H-5, H-8; $^3J_{H,H}$= 9.30 Hz); OH not observed. ^{31}P-NMR (CH_2Cl_2, 121 5 MHz)· δ 110 08 MS *m/z*. 248 ($C_{14}H_{17}O_2P$ 248.3)

2-(1,2-Dimethoxy-4-phenyl)-5-methoxy-4-tert.butyl-1,3-oxaphosphole (16) and 4,6,7-Trimethoxy-2-tert.-butyl-3-phosphanaphthol-1 (17). In the presence of molecular sieve (3Å) a solution of 0.87 g (2.34 mmol) pentacarbonyl[1,2-dimethoxy-4-phenyl(methoxy)carbene]chromium (**15**)[46] and 0.28 g (2.80 mmol) phosphaalkyne **2** in 30 ml DME was warmed to 70° for 4 hr under 5 bar Ar. Removal of the solvent and chromatography of the residue on silica gel using dichloromethane/petroleum ether as eluent gave 0.54 g of a 2/1-mixture of **16/17** which could not be further separated MS *m/z:* 308 ($C_{16}H_{21}O_4P$ 308.3). **16** ^{1}H-NMR ($CDCl_3$, 300.1 MHz). δ 1 33 (d, 9H, C(CH_3)$_3$; $^4J_{P,H}$= 0 86 Hz); 3 87 (s, 3H, OCH_3), 3 90 (s, 3H, OCH_3); 4 03 (s, 3H, OCH_3), 6 81 (d, 1H, H-6', $^3J_{H,H}$= 8.38 Hz); 7,20 (d, 1H, H-3'); 7 26 (dd, 1H, H-5'; $^3J_{H,H}$= 8 25 Hz, $^4J_{H,H}$= 2.24 Hz) ^{13}C-NMR ($CDCl_3$, 75.5 MHz). δ 31 35 (d, C(CH_3)$_3$, $^3J_{P,C}$= 8 30 Hz), 55.81 (s, OCH_3), 58 49 (s, OCH_3), 120 65 (d, C-4, $^1J_{P,C}$= 43 02 Hz), C-1'-C-6' not resolved; 158.20 (d, C-5, $^2J_{P,C}$= 5 28 Hz), 181 44 (d, C-2; $^1J_{P,C}$= 46 04 Hz) ^{31}P-NMR (CH_2Cl_2, 121 5 MHz): δ 110.10 **17** ^{1}H-NMR ($CDCl_3$, 300 1 MHz). δ 1 65 (d, 9H, C(CH_3)$_3$, $^4J_{P,H}$= 2.22 Hz); 3 99 (s, 3H, OCH_3), 4.01 (s, 3H, OCH_3), 4 19 (d, 3H, 4-OCH_3, $^4J_{P,H}$= 2 59 Hz); 7.60 (s, 1H); 7 68 (s, 1H) (H-5, H-8); OH not observed ^{13}C-NMR ($CDCl_3$, 75.5 MHz) δ 31 74 (d, C(CH_3)$_3$; $^3J_{P,C}$= 15 09 Hz), 36 80 (d, C(CH_3)$_3$; $^2J_{P,C}$= 24 90 Hz); 55 87 (s, 6-OCH_3, 7-OCH_3); 58 29 (d, 4-OCH_3, $^3J_{P,C}$= 30 20 Hz); 125.36 (d, C-4a, $^2J_{P,C}$= 5.28 Hz), 140.13 (d, C-2; $^1J_{P,C}$= 50.56 Hz); 147 03 (d, C-1, $^2J_{P,C}$= 12 53 Hz); 186.75 (d, C-4, $^1J_{P,C}$= 44.52 Hz); C-5-C-8 not resolved ^{31}P-NMR (CH_2Cl_2, 121 5 MHz): δ 101 48

2-(2'-Furyl)-5-methoxy-4-tert.butyl-1,3-oxaphosphole (19) and 4-hydroxy-7-methoxy-5-tert.butyl-6-phosphabenzofuran (20). A solution of 1 00 g (3.30 mmol) pentacarbonyl[2-furyl- (methoxy)carbene]chromium (**18**)[47] and 0.42 g (4.20 mmol) phosphaalkyne **2** in 40 ml DME was warmed to 90° for 3 hr under a pressure of 9 bar Ar while a gentle stream of Ar was bubbled through the vessel to remove cleaved CO. Monitoring of the reaction by ^{1}H-NMR indicated that oxaphosphole **19** and the chromium-coordinated phosphabenzofuran

20 • $Cr(CO)_3$ had formed in an approximately 1/2 ratio. Chromatographic workup on silica gel at -25° using dichloromethane/petroleum ether (1/3 to 1/0) gave first a yellow powder of **19**. The following red band contained the coordinated phosphabenzofuran. To avoid uncontrolled decomposition it was warmed in boiling toluene for 3 hr; column chromatography at -25° (petroleum ether/ether 5/1) gave a yellow powder of **20** along with (toluene)$Cr(CO)_3$. **19**: 0.17 g (22%). ^{1}H-NMR (CD_3COCD_3, 300.1 MHz): δ 1.32 (d, 9H, $C(CH_3)_3$, $^4J_{P,H}$= 1.44 Hz); 4.06 (s, 3H, OCH_3); 6 56 (m, 1H, H-3'); 6.63 (m, 1H, H-4'); 7.56 (m, 1H; H-5'). ^{13}C-NMR (CD_3COCD_3, 75.5 MHz): δ 31.62 (d, $C(CH_3)_3$; $^3J_{P,C}$= 7.83 Hz); 32.09 (d, $C(CH_3)_3$; $^2J_{P,C}$= 14 70 Hz), 59.25 (s, OCH_3); 104.86 (d, C-3'; $^3J_{P,C}$= 12.53 Hz); 112.64 (s, C-4'); 122.97 (d, C-4; $^1J_{P,C}$= 44.37 Hz); 143.08 (d, C-5'; $^5J_{P,C}$= 4.75 Hz); 151.38 (d, C-2'; $^2J_{P,C}$= 12.00 Hz); 159.53 (d, C-5; $^2J_{P,C}$= 6.18 Hz); 172.25 (d, C-2; $^1J_{P,C}$= 46.41 Hz). ^{31}P-NMR (CD_3COCD_3, 121.5 MHz): δ 113.41. MS *m/z:* 238 (Found: C, 60.34; H 6.22%; $C_{12}H_{15}O_3P$ 238.2. Requires: C, 60.50; H., 6.35%). **20**: 0.07 g (9%). ^{1}H-NMR (CD_3COCD_3, 300.1 MHz). δ 1.56 (d, 9H, $C(CH_3)_3$; $^4J_{P,H}$= 2.59 Hz); 4.08 (d, 3H, OCH_3; $^4J_{P,H}$= 2.05 Hz); 7.24 (s, br, 1H, H-4'); 7.81 (s, br, 1H, H-5'); 8.45 (s, 1H, OH). ^{13}C-NMR (CD_3COCD_3, 75.5 MHz). δ 31 71 (d, $C(CH_3)_3$; $^3J_{P,C}$= 15.98 Hz); 38.56 (d, $C(CH_3)_3$; $^2J_{P,C}$= 25.28 Hz); 58.71 (d, OCH_3; $^3J_{P,C}$= 29 60 Hz); 106.72 (d, C-2; $^4J_{P,C}$= 3.72 Hz); 126.22 (d, C-7a, $^2J_{P,C}$= 6.74 Hz); 144.92 (d, C-3; $^4J_{P,C}$= 5 93 Hz); 148.25 (d, C-3a; $^3J_{P,C}$= 14.59 Hz); 148.57 (d, C-4; $^2J_{P,C}$= 10 56 Hz); 148.97 (d, C-5; $^1J_{P,C}$= 57.25 Hz); 173.03 (d, C-7; $^1J_{P,C}$= 51.61 Hz). ^{31}P-NMR (CD_3COCD_3, 121 5 MHz): δ 120.19. MS *m/z:* 238 ($C_{12}H_{15}O_3P$ 238.2).

5-Ethoxy-2-(2'-thienyl)-4-tert.butyl-1,3-oxaphosphole (22) and tricarbonyl(3a-7a-η^6-7-ethoxy-4-hydroxy-5-tert.butyl-6-phosphabenzothiophene)chromium (23). A solution of 1 48 g (4.45 mmol) pentacarbonyl[ethoxy(2-thienyl)carbene]chromium (**21**)[48] and 0.60 g (6 00 mmol) phosphaalkyne **2** in 35 ml ether was kept at 90° for 3 hr under 9 bar Ar as described above. Chromatographic workup on silica gel at -25° using dichloromethane/petroleum ether (1/1) and ether as eluents gave a black oil of **22** and red crystals of **23.** **22**: 0.51 g (43%). ^{1}H-NMR ($CDCl_3$, 300.1 MHz): δ 1.30 (d, 9H, $C(CH_3)_3$; $^4J_{P,H}$= 1.26 Hz); 1.41 (t, 3H, CH_3CH_2O; $^3J_{H,H}$= 7 04 Hz); 4.30 (q, 2H, CH_3CH_2O; $^3J_{H,H}$= 7.08 Hz); 6.94 (ddd, 1H, H-3'); $^3J_{H,H}$= 4.31 Hz, $^4J_{H,H}$= 1.06 Hz); 7.12 (d, 1H, H-4'; $^3J_{H,H}$= 4.80 Hz); 7.23 (m, 1H, H-5'). ^{13}C-NMR ($CDCl_3$, 75 5 Hz): δ 15.18 (s, CH_3CH_2O); 31.41 $C(CH_3)_3$; $^3J_{P,C}$= 7.90 Hz); 67.73 (s, CH_3CH_2O); 121.19 (d, C-4; $^1J_{P,C}$= 45 56 Hz), 121 41 (d, C-3'; $^3J_{P,C}$= 12.53 Hz); 123.69 (d, C-5', $^5J_{P,C}$= 6.79 Hz); 127.70 (d, C-4'; $^4J_{P,C}$= 1.88 Hz); 138.73 (d, C-2'; $^2J_{P,C}$= 14.86 Hz); 157.59 (d, C-5, $^2J_{P,C}$= 5.88 Hz), 175.30 (d, C-2; $^1J_{P,C}$= 44.68 Hz). ^{31}P-NMR (CH_2Cl_2, 121.5 MHz). δ 113.04. MS *m/z:* 268. ($C_{13}H_{17}O_2PS$ 268 3). **23** 0.08 g (4%). ^{1}H-NMR (CD_3COCD_3, 300 1 MHz): δ 1.44 (d, 9H, $C(CH_3)_3$; $^4J_{P,H}$= 2.72 Hz); 4.00 (dq, 1H; $^3J_{H,H}$= 7.06 Hz, $^4J_{H,H}$= 1.70 Hz), 4.26 (dq, 1H; $^3J_{H,H}$= 7 06 Hz, $^4J_{H,H}$= 1.70 Hz) (CH_3CH_2O); 7.88 (d, 1H, H-4'; $^3J_{H,H}$= 5.67 Hz); 7 99 (d, 1H, H-5'; $^3J_{H,H}$= 5.68 Hz); OH not observed. ^{13}C-NMR (CD_3COCD_3, 75 5 MHz). δ 14.99 (d, CH_3CH_2O, $^4J_{P,C}$= 2.96 Hz); 31.68 (d, $C(CH_3)_3$, $^3J_{P,C}$= 14 56 Hz), 37.80 (d, $C(CH_3)_3$, $^2J_{P,C}$= 19 75 Hz); 68.92 (d, CH_3CH_2O; $^3J_{P,C}$= 27 94 Hz), 110 96 (d, C-5; $^1J_{P,C}$= 71.03 Hz); 104 10 (s), 115.96 (d, $J_{P,C}$= 8.15 Hz), 123.64 (s), (C-2-C-3a), 132.16 (s, C-4); 147 93 (d, C-7; $^1J_{P,C}$= 73 75 Hz), 234 16 (s, $Cr(CO)_3$). ^{31}P-NMR (CD_3COCD_3, 121.5 MHz) δ -27 55 MS *m/z:* 404. ($C_{16}H_{17}CrO_4PS$ 404 4).

Pentacarbonyl[2,3-dimethyl-4-methoxy-1-(2-tert.butylketenyl)-1,2-dihydrophosphete]chromium (24). A solution of 1.56 g (5.37 mmol) pentacarbonyl[*Z*-2-butenyl(methoxy)carbene]chromium (**1b**)[44] and 0.61 g (6.10 mmol) phosphaalkyne **2** in 20 ml *tert.*BuOMe was warmed to 70° for 7 hr under 4 bar Ar. Chromatographic work up at -25° using dichloromethane/petroleum ether (1/5) as eluent gave several bands two of which contained the yellow phosphinine complex **3** and the orange 1,2-dihydrophosphete complex **24** **24**. 0 11 g (5%). IR (C_6H_{14}, ν_{CO} cm^{-1}) 2095 m [C=C=O], 2060 m, 1955 vs, sh, 1945 vs [$Cr(CO)_5$] ^{1}H-NMR ($CDCl_3$, 300.1 MHz). δ 1 30 (s, 9H, $C(CH_3)_3$); 1.27 (dd, 3H, 2-CH_3; $^3J_{H,H}$= 9.9 Hz, $^3J_{P,H}$= 16 1 Hz); 1.79 (d, 3H, 3-CH_3, $^4J_{H,H}$= 1 1 Hz), 2 54 (m, 1H, H-2); 3 90 (s, 3H, OCH_3); ^{13}C-NMR ($CDCl_3$, 75.5 MHz)· δ 13 09 (d, 2-CH_3; $^2J_{P,C}$= 15.7 Hz), 13.92 (d, 3-CH_3; $^3J_{P,C}$= 4.4 Hz); 29 72 (s, *C*=C=O); 31 64 (d, $C(CH_3)_3$, $^3J_{P,C}$= 2.2 Hz); 33 29 (d, $C(CH_3)_3$, $^2J_{P,C}$= 3 3 Hz); 39.55 (d, C-2, $^1J_{P,C}$= 31 3 Hz), 59 05 (d, OCH_3; $^3J_{P,C}$= 6 3 Hz), 124 09 (d, C-3; $^3J_{P,C}$= 10.1 Hz), 148 28 (d, C-4 $^1J_{P,C}$= 50.6 Hz); 184 20 (d, =C=*C*=O, $^2J_{P,C}$= 14 8 Hz); 216.20 (d, *cis*-CO; $^2J_{P,C}$= 13.4 Hz), 221.12 (d, *trans*-CO, $^2J_{P,C}$= 6.9 Hz) ^{31}P-NMR ($CDCl_3$, 121 5 MHz). δ 72 72. MS *m/z:* 418 ($C_{17}H_{19}CrO_7P$ 418 3)

2-(1',4'-Dimethoxy-2'-naphthyl)-5-methoxy-4-tert.butyl-1,3-oxaphosphole (26). A solution of 1.09 g (2 76 mmol) tetracarbonyl[1,4-dimethoxy-2-naphthyl(methoxy)carbene-*C,O*]chromium (**25**)[49] and 0.30 g (3.00 mmol) phosphaalkyne **2** in 50 ml *tert*.BuOMe was warmed to 70° for 3 hr under 5 bar Ar. Removal of the solvent and chromatographic workup (silica gel, -25°, dichloromethane/petroleum ether 1/3 to 1/0) afforded 0 25 g of starting material **25** and a non-separable mixture of **26** and pentacarbonyl complex **27**. The latter was modified into aminocarbene complex **28** via aminolysis with 5 ml n-propylamine in 10 ml petroleum ether at 0°. Chromatography on silica gel using dichloromethane/petroleum ether 1/3 gave first oxaphosphole **26** as a yellow solid followed by aminocarbene complex **28**. **26**: 0 11 g (11%) ^{1}H-NMR ($CDCl_3$, 300.1 MHz): δ 1.37 (d, 9H, $C(CH_3)_3$; coupling not resolved); 3.92 (s, 3H), 4.00 (s, 3H), 4.08 (s, 3H) (1'-, 4'-, 5-OCH_3); 7 18 (s, 1H, H-3'); 7.42 (dd, 1H, $^3J_{H,H}$= 8.08 Hz), 7.52 (dd, 1H; $^3J_{H,H}$= 7.50 Hz) (H-6', H-7'); 8.03 (d, 1H, H-5'; $^3J_{H,H}$= 8.38 Hz), 8.18 (d, 1H, H-8'; $^3J_{H,H}$= 8 31 Hz). ^{13}C-NMR ($CDCl_3$, 75 5 MHz): δ 31.43 (d, $C(CH_3)_3$; $^3J_{P,C}$= 7 82 Hz); 31.72 (d, $C(CH_3)_3$; $^2J_{P,C}$= 14 31 Hz), 55 57 (s), 58.28 (s), 59 58 (d; $J_{P,C}$= 7.34 Hz) (1'-, 4'-, 5-OCH_3); 122.91 (d, C-4, $^1J_{P,C}$= 46.79 Hz); 98.70 (d, $J_{P,C}$= 8.68 Hz), 103 17 (s); 122 42 (s); 123.45 (d; $J_{P,C}$= 5.66 Hz); 125.34 (d, $J_{P,C}$= 1.58 Hz), 125.79 (d, $J_{P,C}$= 2 72 Hz); 126.91 (s); 128 84 (s); 145.80 (d; $J_{P,C}$= 4.75 Hz); 151 95 (s) (C-1'-C-8'); 158.16 (d; $^2J_{P,C}$= 5.43 Hz); 175.01 (d; $^1J_{P,C}$= 56.67 Hz) ^{31}P-NMR (Et_2O, 121.5 MHz): δ 141.85. MS *m/z:* 358. ($C_{20}H_{23}O_4P$ 358.4).

(1-Methoxy-2-phenyl)-5-methoxy-4-tert.butyl-1,3-oxaphosphole (30). A solution of 0.47 g (1.51 mmol) tetracarbonyl[methoxy(1-methoxy-2-phenyl)carbene-*C,O*]chromium (**29**)[49] and 0.24 g (2.40 mmol) phosphaalkyne **2** in 20 ml dichloromethane was kept unter 5 bar Ar at room temperature for 8 hr. Chromatographic workup (silica gel, -25°, dichloromethane/petroleum ether 1/3) gave **30** as a dark red oil. **30**: 0.25 g (60%). ^{1}H-NMR ($CDCl_3$, 300.1 MHz)· δ 1.35 (d, 9H, $C(CH_3)_3$; $^4J_{P,H}$= 0.84 Hz); 3.97 (s, 3H), 4.03 (s, 3H) (1'-, 5-OCH_3); 6.95 (dd, 1H, H-6'; $^3J_{H,H}$= 8.23 Hz); 6.98 (dd, 1H, H-4', $^3J_{H,H}$= 7.39 Hz); 7.18 (dd, 1H, H-5'; $^3J_{H,H}$= 7.80 Hz); 7.77 (d, 1H, H-3'; $^3J_{H,H}$= 7.65 Hz) ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 31.30 (d, $C(CH)_3$)$_3$, $^3J_{P,C}$= 7.86 Hz); 31.54 (not resolved); 54 92 (s), 57 92 (s) (1'-, 5-OCH_3); 110.54 (s, C-6'); 120.40 (s, C-4'); 121.46 (d, C-4, $^1J_{P,C}$= 47.32 Hz); 122.66 (d, C-3'; $^3J_{P,C}$= 10.94 Hz); 124.06 (d, C-2'; $^2J_{P,C}$= 5 74 Hz), 127.27 (d, C-5'; $^4J_{P,C}$= 4.30 Hz), 155.58 (s, C-1'); 158.01 (d, C-5; $^2J_{P,C}$= 5.21 Hz); 174 22 (d, C-2, $^1J_{P,C}$= 58.87 Hz) ^{31}P-NMR (CH_2Cl_2, 121 5 MHz)· δ 137.6, MS *m/z:* 278. ($C_{15}H_{19}O_3P$ 278 3).

Pentacarbonyl[(1-methoxy-2-phenyl)-5-methoxy-4-tert.butyl-1,3-oxaphosphole]chromium (31) and pentacarbonyl[2-(η^6-1-methoxy-2-phenyl-tricarbonylchromium)-5-methoxy-4-tert.butyl-1,3-oxaphosphole]-chromium (32). A solution of 0.39 g (1.40 mmol) oxaphosphole **30** and an excess of $Cr(CO)_5$• THF in 10 ml THF was warmed to 70° for 30 min. Chromatographic workup (silica gel, -25°, dichloromethane/petroleum ether 1/3) afforded first **31** followed by **32** as orange powders. **31**: 0.18 g (27%). IR (C_6H_{14}, ν_{CO} cm^{-1}). 2078 m, 1990 w, 1957 vs. ^{1}H-NMR (CD_3COCD_3, 300.1 MHz): δ 1 44 (d, 9H, $C(CH_3)_3$; $^4J_{P,H}$= 0 55 Hz); 3.82 (s, 3H), 3 97 (s, 3H) (1'-, 5-OCH_3); 6.95 (d, 1H, H-6'; $^3J_{H,H}$= 8 37 Hz); 7.00 (dd, 1H, H-4'; $^3J_{H,H}$= 7 50 Hz), 7 40 (d, 2H, H-3', H-5'; coupling not resolved) ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 31.71 (d, $C(CH_3)_3$, $^3J_{P,C}$= 5 20 Hz), 32 30 (d, $C(CH_3)_3$; $^2J_{P,C}$= 10.80 Hz); 55 67 (s), 57.99 (s) (1'-, 5-OCH_3); 111 26 (s, C-6'), 121 26 (d, C-4, $^1J_{P,C}$= 11.17 Hz); 117.73 (s), 120 29 (s), 131 36 (s), 132.15 (d; $^2J_{P,C}$= 9 51 Hz) (C-2'-C-5'), 157 67 (d, C-1', $^3J_{P,C}$= 7.40 Hz); 160 94 (d, C-5; $^2J_{P,C}$= 3 40 Hz); 176.65 (d, C-2; $^1J_{P,C}$= 30.26 Hz); 214 88 (d, *cis*-CO; $^2J_{P,C}$= 15.24 Hz), 221 36 (d, *trans*-CO; $^2J_{P,C}$= 3 90 Hz) ^{31}P-NMR (CH_2Cl_2), 121 5 MHz) δ 135 50 MS *m/z:* 470. ($C_{20}H_{19}CrO_8P$ 470.3). **32**. 0.18 g (21%) IR (C_6H_{14}, ν CO cm^{-1}) 2078 m, 1975 m, 1957 vs, 1900 m. ^{1}H-NMR ($CDCl_3$, 300 1 MHz)· δ 1.40 (d, 9H), $C(CH_3)_3$); 3.75 (s, 3H), 4.06 (s, 3H), (1'-, 5-OCH_3), 4.90 (br, 1H, H-6'); 5.05 (br, 1H, H-4'); 5.67 (br 1H, H-5'); 5.84 (br, 1H, H-3') ^{13}C-NMR ($CDCl_3$, 75 5 MHz) δ 31.47 (d, $C(CH_3)_3$; $^3J_{P,C}$= 4.95 Hz); 32.36 (d, $C(CH_3)_3$; $^2J_{P,C}$= 10 40 Hz), 55 92 (s), 57 87 (s) (1'-, 5-OCH_3); 72 08 (s), 83 30 (s), 95.30 (s), 99.49 (d, $J_{P,C}$= 8.34 Hz), 142 43 (d, $^3J_{P,C}$= 7 04 Hz) (C-1'-C-6', 1 signal not observed); 160 97 (s, C-5), 168.91 (d, C-2, $^1J_{P,C}$= 32 10 Hz), 214 69 (d, *cis*-CO; $^2J_{P,C}$= 15.00 Hz); 220.48 (br, *trans*-CO), 232 33 (s, $Cr(CO)_3$). ^{31}P-NMR (CH_2Cl_2, 121 5 MHz) δ 151.2 MS *m/z* 606 ($C_{23}H_{19}Cr_2O_{11}P$ 606 4).

5-Ethoxy-2-(η^6-1-methoxy-2-phenyl-tricarbonylchromium)-4-tert.butyl-1,3-oxaphosphole (34). A solution of 1 08 g (2 33 mmol) tetracarbonyl[η^6-1-methoxy-2-phenyl-tricarbonylchromium(ethoxy)carbene-*C,O*]-

chromium (**33**)[50] and 0.31 g (3.10 mmol) phosphaalkyne **2** in 50 ml ether was warmed to 70° for 1 hr under 5 bar Ar. Chromatography on silica gel (-25°, dichloromethane/petroleum ether 1/2) followed by recrystallization from dichloromethane/petroleum ether (1/3) gave red crystals. **34**: 0.76 g (77%) IR (C_6H_{14}, ν_{CO} cm^{-1}): 1957 vs, 1880 vs ^{1}H-NMR (CD_3COCD_3, 300.1 MHz): δ 1 37 (d, 9H, $C(CH_3)_3$; $^4J_{P,C}$= 1.48 Hz); 1 50 (t, 3H, CH_3CH_2O, $^3J_{H,H}$= 7.09 Hz); 4.02 (s, 3, OCH_3); 4.51 (q, 2H, CH_3CH_2O; $^3J_{H,H}$= 7.03 Hz), 5.32 (dd, 1H, H-6'; $^3J_{H,H}$= 6.38 Hz); 5.80 (d, 1H, H-4'; $^3J_{H,H}$= 6.30 Hz); 5.90 (ddd, 1H, H-5'; $^3J_{H,H}$= 6.56 Hz, $^2J_{H,H}$= 1.16 Hz); 6.57 (d, 1H, H-3'; $^3J_{H,H}$= 6.57 Hz). ^{13}C-NMR (CD_3COCD_3, 75.5 MHz): δ 15.47 (s, CH_3CH_2O); 31.67 (d, $C(CH_3)_3$; $^3J_{P,C}$= 7.77 Hz); 32.25 (d, $C(CH_3)_3$, $^2J_{P,C}$= 14.36 Hz); 56.52 (s, OCH_3); 68.39 (s, CH_3CH_2O); 76.88 (s, C-6'); 86.88 (s), 92.13 (d, $^1J_{P,C}$= 7.28 Hz); 94.34 (d, $J_{P,C}$= 9.08 Hz); 95.13 (s) (C-2'-C-5'); 123.23 (d, C-4; $^1J_{P,C}$= 47.85 Hz); 140.86 (s, C-1'); 159.18 (d, C-5; $^2J_{P,C}$= 5.74 Hz); 171.36 (d, C-2, $^1J_{P,C}$= 59.18 Hz); 234.81 (s, $Cr(CO)_3$). ^{31}P-NMR (CH_2Cl_2, 121.5 MHz): δ 143.00 MS *m/z:* 428 (Found: C, 53.03; H, 5.14% $C_{19}H_{21}CrO_6P$ 428 3 Requires: C, 53, 28; H, 4.94%)

X-Ray structure determinations

3: $C_{15}H_{19}CrO_5P$ (M_r= 362.5): Mo-K_α radiation, λ= 0.71069 Å graphite monochromator, Enraf-Nonius CAD4 diffractometer, space group $P2_1/c$ (No.14) with a=13.098(1), b=7.615(1), c=17.463 (1) Å, β= 110.06 (1)°, V=1636.1(3) Å^3, D_c=1 471 g/cm^3, F(000)=752, T=-65°C. 4906 Reflections (h ±17, k -10, +1, l ±22), 3760 unique (R_{int}=0.0245), 3500 observed (F>5σ(F)). Correction of the data with DIFABS[51]. R(wR)=0.0309(0.0356), w=1/σ^2(Fo), for 275 refined parameters (non hydrogens anisotropic, hydrogens isotropic, Siemens SHELXTL PLUS (VMS)). Residual electron density: 0.45 eÅ^{-3}. The final atomic coordinates are given in Table. 1. Further details of the crystal structure determination are available from the Cambridge Crystallographic Data Centre, University Chemical Lab., Lensfield Road, Cambridge GB2 1EW, U.K. Requests should be accompanied by a full literature citation

Expertimental data for **5a** and **34** are given in ref 26. Further details have been deposited at the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2 [depository numers CSD-52863 (**5a**) and CSD-53363 (**34**)].

Table 1· Atomic coordinates (x10^4) and equivalent isotropic displacement coefficients (Å^{2}x10^3) for **3**

	x	y	z	U(eq)
Cr	2470(1)	2302(1)	9782(1)	20(1)
P	1229(1)	3019(1)	10522(1)	25(1)
O(1)	4078(1)	5496(2)	10869(1)	29(1)
O(2)	-137(1)	3296(2)	8959(1)	33(1)
O(3)	3184(1)	-923(2)	10807(1)	44(1)
O(4)	4494(1)	1820(2)	9378(1)	40(1)
O(5)	1281(1)	-39(2)	8383(1)	54(1)
C(1)	863(1)	3738(2)	9505(1)	24(1)
C(2)	1509(1)	4699(2)	9144(1)	23(1)
C(3)	2586(1)	5193(2)	9605(1)	22(1)
C(4)	3052(1)	4884(2)	10465(1)	21(1)
C(5)	2571(1)	3880(2)	10924(1)	22(1)
C(6)	2906(1)	336(2)	10425(1)	28(1)
C(7)	3708(1)	2030(2)	9533(1)	25(1)
C(8)	1748(2)	872(3)	8916(1)	31(1)
C(9)	3265(2)	6200(3)	9202(1)	31(1)
C(10)	993(2)	5209(3)	8256(1)	36(1)
C(11)	3156(2)	3600(2)	11854(1)	28(1)
C(12)	2547(2)	2253(3)	12196(1)	40(1)
C(13)	4329(2)	2935(3)	12082(2)	39(1)
C(14)	3130(2)	5371(3)	12272(1)	36(1)
C(15)	-762(2)	2036(3)	9208(2)	44(1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 2. Atomic coordinates and equivalent isotropic displacement coefficients ($Å^2$) for 5a

	x	y	z	B(eq)
Cr	0.18001(4)	0.27500(4)	0.91560(2)	2.274(7)
P1	-0.03950(6)	0.22400(6)	0.83271(4)	2.66(1)
O1	-0.0908(2)	0.2122(2)	0.9846(1)	3.57(4)
O2	0.3005(2)	0.0626(2)	0.8184(1)	3.73(4)
O3	0.4696(2)	0.3075(2)	0.9221(2)	6.18(6)
O4	0.1126(2)	0.4998(2)	0.8348(1)	4.52(5)
O5	0.1983(2)	0.4018(2)	1.0746(1)	6.31(6)
C1	0.0993(2)	0.1735(2)	0.7967(1)	2.55(5)
C2	0.1974(2)	0.1084(2)	0.8476(1)	2.60(5)
C3	0.2064(2)	0.0829(2)	0.9342(1)	2.53(5)
C4	0.3155(3)	0.0118(2)	0.9737(2)	3.20(6)
C5	0.3318(3)	-0.0185(2)	1.0537(2)	3.76(7)
C6	0.2477(3)	0.0239(2)	1.1054(2)	3.29(6)
C7	0.2763(3)	-0.0034(3)	1.1908(2)	4.24(7)
C8	0.2017(3)	0.0409(3)	1.2428(2)	4.97(8)
C9	0.0979(3)	0.1124(3)	1.2112(2)	5.31(8)
C10	0.0667(3)	0.1400(3)	1.1276(2)	4.41(7)
C11	0.1404(2)	0.0951(2)	1.0716(2)	2.99(6)
C12	0.1134(2)	0.1211(2)	0.9811(1)	2.49(5)
C13	-0.0012(2)	0.1818(2)	0.9376(1)	2.57(5)
C14	0.1011(3)	0.1980(2)	0.7038(1)	2.95(6)
C15	0.3584(3)	0.2955(2)	0.9199(2)	3.52(6)
C16	0.2329(3)	0.2524(2)	0.6928(2)	3.79(7)
C17	0.1402(2)	0.4120(2)	0.8648(2)	2.93(6)
C18	0.1935(3)	0.3515(2)	1.0139(2)	3.48(6)
C19	-0.0081(3)	0.2826(3)	0.6659(2)	4 22(7)
C20	0.0719(3)	0.0859(3)	0.6547(2)	3.98(7)
C21	-0.1876(3)	0.2961(3)	0.9532(2)	5.87(8)

Isotropic equivalent displacement parameter defined as:

(4/3) * [a^2*B(1,1) + b^2*B(2,2) + c^2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)]

Table 3 Atomic coordinates ($x10^4$) and equivalent isotropic displacement coefficients ($Å^2x10^3$) for 34

	x	y	z	U(eq)
Cr(1)	8412(1)	2388(1)	4018(1)	40(1)
P(1)	8026(1)	-1296(2)	1914(1)	47(1)
O(1)	6897(2)	1190(5)	2214(1)	53(1)
O(2)	5577(2)	371(6)	1538(2)	89(2)
O(3)	9490(2)	-184(5)	3010(1)	50(1)
O(4)	6546(2)	1209(7)	3958(2)	103(2)
O(5)	8499(3)	4169(6)	5411(2)	90(2)
O(6)	9000(2)	-1376(6)	4757(2)	72(2)
C(1)	6903(3)	-1465(8)	1486(2)	43(2)
C(2)	6441(3)	-42(8)	1729(2)	53(2)
C(3)	7773(3)	689(7)	2370(2)	39(2)
C(4)	8308(3)	1997(6)	2863(2)	37(2)
C(5)	9190(3)	1566(8)	3193(2)	40(2)
C(6)	9681(3)	2867(8)	3673(2)	47(2)
C(7)	9325(3)	4675(8)	3807(2)	55(2)
C(8)	8469(3)	5216(7)	3467(2)	53(2)
C(9)	7963(3)	3872(8)	3017(2)	48(2)
C(10)	6517(3)	-2958(8)	935(2)	56(2)
C(11)	7214(4)	-4455(10)	841(3)	109(3)
C(12)	6193(5)	-1911(10)	256(2)	120(3)
C(13)	5763(4)	-4113(10)	1129(3)	109(3)
C(14)	5131(3)	1223(9)	1997(3)	75(2)
C(15)	4186(3)	1348(9)	1745(3)	78(2)
C(16)	10344(3)	-813(7)	3350(2)	55(2)
C(17)	7267(3)	1675(8)	3987(2)	61(2)
C(18)	8456(3)	3519(7)	4869(2)	56(2)
C(19)	8774(3)	68(8)	4473(2)	46(2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

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