1,3-Diphospholene-4-ylidene Chromium (Tungsten) Pentacarbonyl Complexes Formed by CO Insertion into the Ring of a 1,3-Diphosphacyclobutane-2,4-diyl-2-ide—Complexes of a Phosphanyl Carbene or a Phosphonium Ylide?

André Fuchs,[a] Dietrich Gudat,[a] Martin Nieger,[a] Olaf Schmidt,[a] Manuel Sebastian,[a] Laszlo Nyulaszi,[b] and Edgar Niecke*[a]

Dedicated to Professor Manfred Regitz—a pioneer in the chemistry related to the phosphorus–carbon diagonal relationship—on the occasion of his 66th birthday

Abstract: Reaction of the 1,3-diphosphacyclobutane-2,4-diyl-2-ide **1** with chromium or tungsten hexacarbonyl afforded the anionic complexes [*cyclo*-{P(Mes*)-C(SiMe$_3$)-P(Mes*)-C(O)-C[M(CO)$_5$]}]$^-$ (**3a**,**b**: M = Cr, W) by the formal insertion of CO into the four membered ring. Computational analysis suggests that this reaction proceeds via two intermediates that can be formulated as a cyclic metal acyl and an acyclic ketenyl complex. The anionic complexes **3a**,**b** further reacted with electrophiles to afford the neutral complexes [*cyclo*-{P(Mes*)-C(SiMe$_3$)-P(Mes*)-C(OR)-C[M(CO)$_5$]}] (**4a**,**b**: M = Cr, W, R = Me; **5**, **6**: M = Cr, R = SiMe$_3$, H). All products were characterized by standard spectroscopic (NMR and MS) techniques, and **4a**,**b** further by extensive one- and two-dimensional multinuclear (^{1}H, ^{13}C, ^{31}P, ^{183}W) NMR studies. From these investigations, an unequivocal assignment of chemical shifts and coupling constants was derived, confirming unusually large shielding for the formal carbenic carbon atoms which exceed even those in complexes of imidazoyl carbenes. Single-crystal X-ray diffraction analyses of **3a**, **4a**,**b**, and **5** revealed that all of these compounds contain planar P_2C_3 rings. The phosphorus atoms are slightly pyramidal, and the carbon–metal distances (C – Cr 218 pm, C – W 230 pm) suggest low bond orders. Comparison of the structural parameters of **3a** with those of the O-substitution products **4a**, **5** revealed substantial changes in endocyclic P – C bond lengths and the degree of pyramidal character of bonding at the phosphorus atoms. In line with the spectroscopic and computational results, these effects were interpreted in terms of a considerable reorganization of π electrons in the ring, which induces a substantial degree of aromatic character in the neutral complexes **4**–**6**.

Keywords: computer chemistry · insertion · NMR spectroscopy · carbene complexes · phosphorus heterocycles

Introduction

Stable compounds containing a divalent carbon atom can be obtained if the subvalent center is stabilized by *push–pull* substituent effects as in "Bertrand-type"[1] (**I**) (Scheme 1) or by π-donor (*push*) substituents as in "Arduengo-type" compounds (**II**).[2] The carbene-like reactivity of **I** may be observed in many examples,[3] and such systems can consequently be considered as crypto-carbenes. However, the synthesis of a transition metal complex with a crypto-carbene ligand of this type has not been reported. According to recent theoretical studies by Schoeller et al.,[4] the reason for this behavior is the high distortion energy associated with the contraction of the obtuse valence angle at the divalent carbon atom, which is an essential prerequisite for complexation.

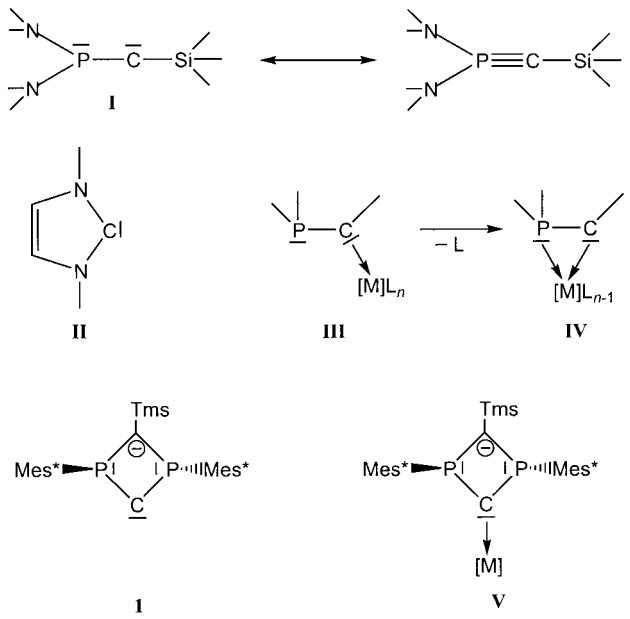
Unstable phosphanyl carbenes (with a *push* substituent) are bent[4, 5] and therefore expected to form metal complexes. Examples of pertinent phosphanyl carbene complexes (**III** in Scheme 1) are known, as reported by Fischer et al.,[6] but generally these compounds are unstable at ambient temperature and transform by means of intermolecular ligand substitution to give complexes of type **IV** (Scheme 1).[7]

The recently synthesized lithium complex of the 1,3-diphosphacyclobutane-2,4-diyl-2-ide **1** (Scheme 1)[8] can be

[a] Prof. Dr. E. Niecke, Dr. A. Fuchs, Prof. Dr. D. Gudat, Dr. M. Nieger, Dr. O. Schmidt, M. Sebastian
Institut für Anorganische Chemie der Universität Bonn
Gerhard-Domagk-Strasse 1, 53121 Bonn (Germany)
Fax: (+49) 228-73-5327
E-mail: e.niecke@uni-bonn.de

[b] Prof. Dr. L. Nyulaszi
Department of Inorganic Chemistry
Technical University of Budapest
Gellért tér 4, 1521 Budapest (Hungary)

  0947-6539/02/0809-2188 $ 20.00+.50/0



Scheme 1. Mes* = 2,4,6-*t*Bu$_3$C$_6$H$_2$; Tms = SiMe$_3$.

Abstract in German: *Die Reaktion des 1,3-Diphosphacyclobutan-2,4-diyl-2-ids* ***1*** *mit [Cr(CO)$_6$] bzw. [W(CO)$_6$] verläuft unter einer formalen Insertion von CO in den Vierring unter Ausbildung der anionischen Komplexe [cyclo-{P(Mes*)-C(SiMe$_3$)-P(Mes*)-C(O)-C(M(CO)$_5$)}]$^-$ (****3a,b****: M = Cr, W). Theoretischen Berechnungen zufolge sollte die Reaktion über zwei Übergangszustände, einen zyklischen Metall-Acyl- und einen azyklischen Ketenylkomplex verlaufen. Die anionischen Komplexe* ***3a,b*** *bilden bei der Umsetzung mit Elektrophilen neutrale Komplexe [cyclo-{P(Mes*)-C(SiMe$_3$)-P(Mes*)-C(OR)-C(M(CO)$_5$)}] (****4a,b****: M = Cr, W, R = Me;* ***5****,* ***6****: M = Cr, R = SiMe$_3$, H). Alle Produkte wurden durch die üblichen spektroskopischen Methoden (NMR und MS) charakterisiert. Desweiteren wurden ausgiebige ein- und zweidimensionale, multinukleare (^{1}H, ^{13}C, ^{31}P, ^{183}W) NMR-Untersuchungen durchgeführt. Das Ergebnis dieser Studien erlaubt es, ein eindeutiges Zuordnungsschema für die chemischen Verschiebungen und Kopplungskonstanten abzuleiten, und bestätigt die ungewöhnlich große Abschirmung des Kohlenstoffatoms mit formalem Carbencharakter. Diese übertrifft sogar die in Imidazoylkomplexen beobachtete Abschirmung. Einkristall-Röntgenstrukturanalysen von* ***3a****,* ***4a,b*** *und* ***5*** *zeigen, dass alle Verbindungen planare P$_2$C$_3$-Ringe besitzen. Die Phosphoratome sind leicht pyramidalisiert und die Kohlenstoff-Metall-Abstände (C–Cr 218, C–W 230 pm) legen einen geringen Bindungsgrad nahe. Ein Vergleich der Strukturparameter von* ***3a*** *mit denen der O-substituierten Produkte* ***4a****,* ***5*** *zeigt substantielle Änderungen der endozyklischen P–C-Bindungslängen und des Grades der Pyramidalisierung der P-Atome. Zusammen mit den Ergebnissen der spektroskopischen Untersuchungen und der theoretischen Berechnungen werden diese Effekte als eine bemerkenswerte Reorganisation der π-Elektronen des P$_2$C$_3$-Ringes interpretiert, die den neutralen Komplexen* ***4–6*** *einen beträchtlichen, aromatischen Charakter verleiht.*

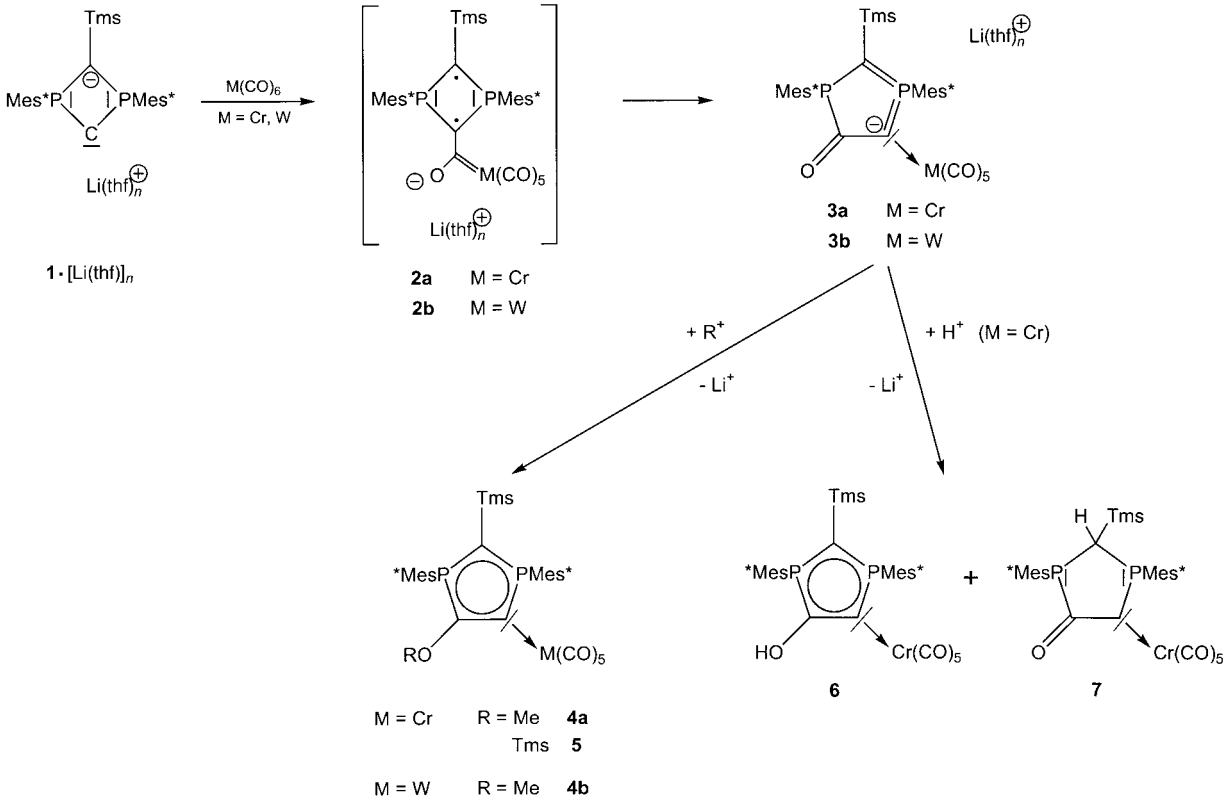
described as an anionic phosphanylcarbene whose valence angle at the carbene carbon atom should be suitable for metal complexation. Therefore, we expected **1** to act as a two-electron donor, forming complexes of type **V**.[9] We now report on complexation reactions of **1** that proceed, surprisingly, by ring expansion to yield products which may formally be addressed as phosphanylcarbene complexes of type **III** (Scheme 1).

Results and Discussion

Syntheses and crystal structure analyses: The lithium salt of 1,3-diphosphacyclobutane-2,4-diyl-2-ide (**1**),[9] prepared by deprotonation of the 1,3-diphosphacyclobutane-2,4-diyl, (Me$_3$Si-CP(Mes*)C(H)P-Mes*),[10] reacts with one equivalent of chromium or tungsten hexacarbonyl to give the anionic complexes **3a**,**b** that were isolated as red crystalline products of the composition [**3a**(**3b**)][Li(thf)$_3$] (Scheme 2). Presumably, this reaction proceeds by the initial formation of intermediates **2a**,**b** by means of the attack of **1** at a carbonyl ligand, and subsequent ring expansion. The proposal of an acyl complex (**2**) as an intermediate is consistent with the formation of similar products during reactions of metal hexacarbonyls with nucleophilic phosphorus ylides.[11]

Subsequent reactions of [**3a**(**3b**)][Li(thf)$_n$] with [Me$_3$O][BF$_4$], and of [**3a**][Li(thf)$_3$] with chlorotrimethylsilane or pyridinium hydrochloride, respectively, yielded the neutral chromium (tungsten) pentacarbonyl complexes **4a**,**b**, **5**, and **6**. These compounds crystallized as red (yellow) solids. The protonation of **3a,b** affords, in addition to **6**, a by-product (10–20%) whose available spectroscopic data are consistent with the formation of a 4-oxo-1,3-diphospholene-5-ylidene complex (**7**) (Scheme 2).[12]

Figure 1 shows the molecular structure of the lithium salt [**3a**][Li(thf)$_3$]. The five-membered P$_2$C$_3$ ring has an "envelope" conformation with the P1 atom sticking out of the plane formed by the other atoms. The lithium atom is surrounded by a distorted tetrahedral array of four oxygen atoms and has a particularly short distance to the keto oxygen atom (Li1 ·· O1 182.7(6) pm). The coordination geometry at the P2 phosphorus atom is characterized by an almost planar (sum of valence angles: 358°) arrangement of substituents and comparatively short endocyclic P–C distances (P2–C3 169.2(3), P2–C2 171.3(3) pm), whereas the P1 phosphorus atom displays a distinctly pyramidal coordination geometry (sum of valence angles: 336°) and significantly longer endocyclic P–C distances (P1–C3 177.1(3), P1–C1 182.1(3) pm). The C1–O1 distance (127.6(3) pm) is similar to bond lengths in carboxylates (125.4 ± 1.0 pm[13]) and ureas (approximately 124 pm[13]). The observed structural features suggest that the bonding in anion **3a** is best described in terms of a canonical structure **A** (Scheme 3; R = Li for **B, C** and **D**) whose heterocyclic ring is composed of adjacent bis(methylene)-phosphorane (C3–P2–C2), phosphane (P1) and carbonyl (C1–O1) fragments (Figure 1). The very long Cr1–C2 bond (218.0(3) pm, as compared to a mean distance of 207 pm for chromium carbene complexes[14]) is remarkable and suggests that the carbene carbon atom has a small degree of π-acceptor



Scheme 2. Mes* = 2,4,6-tBu$_3$C$_6$H$_2$; Tms = SiMe$_3$.

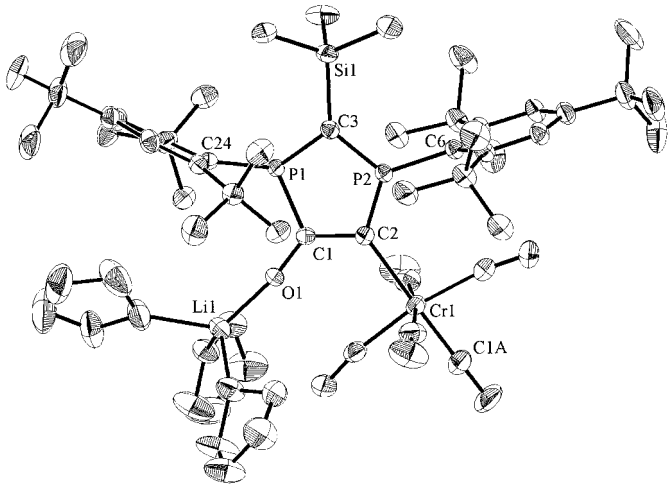
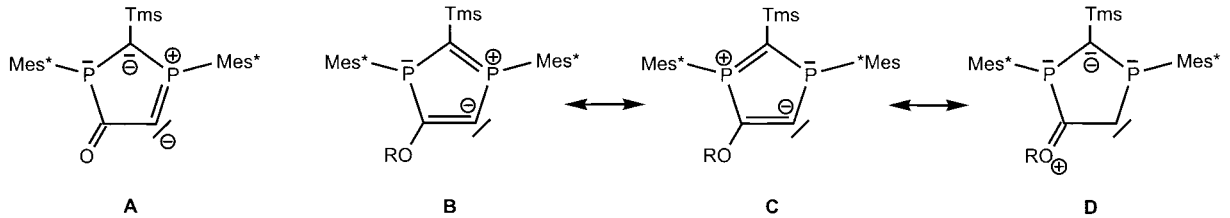


Figure 1. Structure of **3a**. Selected bond lengths [pm] and angles [°]: Cr1–C2 218.0(3), C2–P2 171.3(3), P2–C3 169.2(3), C3–P1 177.1(3), P1–C1 182.1(3), C2–C1 142.5(4), P2–C6 180.9(3), C3–Si1 186.4(3), P1–C24 184.2(3), C1–O1 127.6(3), O1–Li1 182.7(6), Li1–O_{THF} 198.6(7) – 204.5(7), Cr1–C_{cis} 188.2(4) – 190.0(4), Cr1–C1A 182.6(4); P2-C3-P1 100.4(1), C3-P1-C1 102.9(1), P1-C1-C2 112.8(2), C1-C2-P2 106.6(2), C2-P2-C3 113.7(1). (For the sake of comparability of the Figures the CCDC numbering does not conform with the numbering used in this Figure.)

ability. The lengthening of the carbenic Cr1–C2 bond is complimented, as expected, by a shortening of the Cr1–C1A bond positioned *trans* to it (182.6(4) pm vs. 188.2(4) – 190.0(4) pm for Cr1–C_{cis} bonds). Similar bonding is found in the C=Cr(CO)$_5$ fragment in the bis(carbene)chromium complex [{Et$_2$N–C[Cr(CO)$_5$]}$_2$] (Cr–C 219 pm)[15] and an even longer C–Cr bond (226 pm) was observed in a chromium pentacarbonyl complex of the ylidic diphosphete [{(Me$_2$N)$_2$PCH}$_2$].[16]

The molecular structures of the neutral complexes **4a** (Figure 2) and **5** (Figure 3) show almost planar P_2C_3 backbones. Compared to **3a**, the difference in the sums of valence angles at the two phosphorus atoms is less pronounced (**4a**: 343° (P1), 353° (P2); **5**: 345° (P1), 355° (P2)). The P1–C3 distances (**4a**: 173.3(2); **5**: 172.7(3) pm) shorten and the vicinal P2–C2 bonds (**4a**: 174.3(2); **5**: 176.6(3) pm) lengthen in comparison to the corresponding values for **3a**, while the remaining P2–C3 (**4a**: 169.7(2); **5**: 170.7(3) pm) and P1–C1 (**4a**: 179.5(2); **5**: 178.2(3) pm) distances remain similar. Together, these effects result in the tendency for the two geminal and vicinal P–C bonds in the P–C–P and P–C–C–P moieties, respectively, to become equal. A similar tendency is



Scheme 3. Mes* = 2,4,6-tBu$_3$C$_6$H$_2$; Tms = SiMe$_3$; R = Li.

0947-6539/02/0809-2190 $ 20.00+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 9

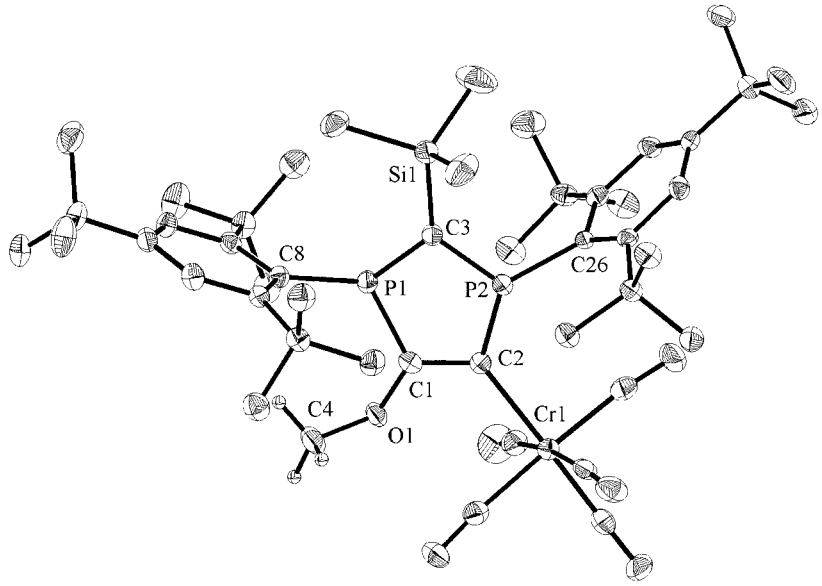


Figure 2. Structure of **4a**, [**4b**]. Selected bond lengths [pm] and angles [°]: C2–P2 174.3(2) [173.8(3)], P2–C3 169.7(2) [169.9(3)], C3–P1 173.3(2) [173.3(3)], P1–C1 179.5(2) [178.8(3)], C1–C2 138.1(3) [138.2(4)], C2–Cr1[W1] 218.3(2) [2.296(3)], P2–C26 180.6(2) [180.2(3)], C3–Si1 188.8(2) [188.7(3)], P1–C8 183.0(2) [182.9(3)], C1–O1 138.0(2) [137.7(4)], O1–C4 142.7(3) [142.5(4)], Cr1–C_{cis} 189.9(3)–190.6(3) [203.1(4)–204.9(4)], Cr1–C1A 184.4(3) [197.7(4)]; C2-C1-P1 116.9(2) [116.7(2)], C1-C2-P2 105.5(2) [106.0(2)], C3-P2-C2 111.5(1) [111.1(2)], P2-C3-P1 102.5(1) [102.6(2)], C3-P1-C1 102.2(1) [102.3(2)].

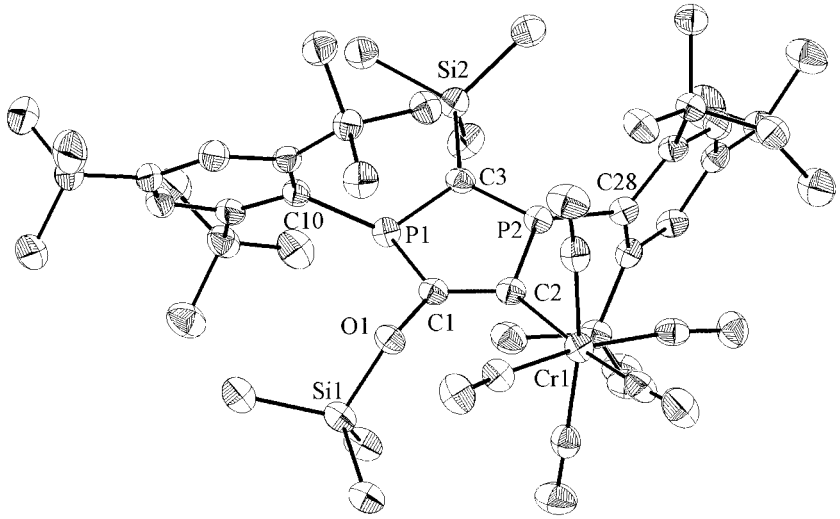


Figure 3. Structure of **5a**. Selected bond lengths [pm] and angles [°]: C2–P2 176.6(3), P2–C3 170.7(3), C3–P1 172.7(3), P1–C1 178.2(3), C1–C2 137.4(4), C2–Cr1 218.9(3), P2–C28 182.5(3), C3–Si2 188.3(3), P1–C10 182.3(3), C1–O1 137.2(3), O1–Si1 168.2(2), Cr1–C_{cis} 188.6(4)–190.0(4), Cr1–C_{trans} 185.6(3), C2-C1-P1 118.0(2), C1-C2-P2 105.8(2), C3-P2-C2 109.8(2), P2-C3-P1 103.7(2), C3-P1-C1 102.3(2).

also observed for the C1–C2 bond (**4a**: 138.1(3); **5**: 137.4(3) pm), which is shorter than the corresponding distance in **3a** (142.5(4) pm) and the C1–O1 distance (**4a**: 138.0(2); **5**: 137.2(3) pm), which is longer than in **3a** (127.6(3) pm); both types of bond fit into the typical ranges of appropriate distances in π-delocalized carbon heterocycles.[13] The metric parameters in the {C[Cr(CO)$_5$]} fragments of both **4a** and **5** agree closely with the corresponding features of **3a**. The molecular structure of the tungsten complex **4b** shows no peculiar dissimilarities with respect to the homologous chromium complex **4a**. The C2–W1 bond length in **4b** is 229.6(3) pm.

Based on the observed structural parameters of **4a**,**b** and **5**, we suggest that the bonding in the five-membered heterocycles of these compounds is best described by a delocalized π-electron system, which can be characterized in terms of the resonance canonical structures **B**–**D** (Scheme 3). Of these, **B** and **C** are considered as dominant, and **D** as being much less important. The emphasis on canonical structures **B** and **C** implies that the ligands in complexes **4a**,**b** and **5**, although formally described as carbenes, should preferably be considered as resonance-stabilized mesoionic species with a considerable degree of formal ylide character at the metal-coordinated carbon atom. The proposed π-electron delocalization is further supported by computed values for the Bird aromaticity index I_5[17] of 0.76 (**4a**) and 0.71 (**5**), respectively. Recently, an aromatic triphosphole with a planar three-coordinate phosphorus atom and a similar Bird index ($I_5 = 0.84$) has been described.[18]

Spectroscopic investigations: In contrast to **1**, the chemical equivalence between the two phosphorus atoms in the five-membered heterocycles of **4**–**6** is lost, and the $^{31}P\{^1H\}$ NMR spectra show two signals which form the parts of an AB spin system and are separated by some 80 ppm ($\delta(^{31}P) = 25-31$ (A-part), 110–135 (B-part)). The coupling constants are very large in all cases; their values lie around 320 Hz for **4**–**6**, but decrease by some 60 Hz in the case of **3**. To achieve an unequivocal assignment of the ^{31}P chemical shifts to the two different sites in the molecule, and to secure the correct identification of the ^1H and ^{13}C NMR signals, we chose the methoxy derivatives **4a,b** to carry out an exhaustive spectroscopic characterization by one- and two-dimensional multinuclear NMR methods. The ^1H and ^{13}C NMR signals of the nuclei in the peripheral Me_3Si, MeO, and CO moieties were easily identified by means of their characteristic chemical shifts. Further assignments were possible from ^1H gs-NOESY spectra, which allowed both the observation of the set of signals belonging to the two Mes*

moieties, and the means of distinguishing between the substituents in 1,3-positions of the ring. This was possible on the basis of characteristic differences in the intensities of cross peaks connecting the resonance signals of protons in these substituents with those of the methoxy group. Measurement of ^{1}H, ^{31}P gs-HMQC spectra allowed us to identify the signal of the phosphorus atom bound to each Mes* group. Accordingly, the less-shielded ^{31}P resonance was assigned to the phosphorus atom adjacent to the metal–carbonyl moiety, and the more shielded one to the phosphorus atom next to the methoxy group. Likewise, ^{1}H, ^{13}C gs-HMQC and HMBC experiments served to identify the signals of all carbon atoms in the Mes* moieties and in the 2- and 5-positions of the central heterocycle. The remaining ^{13}C resonance signal was attributed to the ring-carbon atom next to the metal, as confirmed by two-dimensional ^{31}P-relayed ^{1}H, ^{13}C-HSQC spectra ($\delta(^{13}C) = 162.9$ (**4a**), 152.3 (**4b**), see Figure 4). The pulse scheme used corresponds to a two-dimensional projection of the three-dimensional correlation experiments designed by Rinaldi et al.[19] This is used for the detection of mutually coupled $^{1}H/^{13}C/^{31}P\{^{29}Si\}$ triples in polymers (see Experimental Section for further details) and also yields a precise assignment of individual $J_{P,C}$ coupling constants. Given that the NMR spectra of **3a**,**b**, **5**, and **6** display very similar patterns of chemical shifts and coupling constants to those of **4a** and **4b**, spectral assignments for these compounds were made by analogy with those of **4a** and **4b**. Both ^{31}P NMR signals of the tungsten compounds **3b** and **4b** are accompanied by satellites arising from coupling with the magnetically active ^{183}W isotope ($I = ½$, natural abundance 14.4 %). The $^{2}J_{W,P}$ (25.2 Hz (**3b**); 15.3 Hz (**4b**)) and $^{3}J_{W,P}$ (11.9 Hz (**3b**); 13.8 Hz (**4b**)) coupling constants are similar in magnitude and have, according to the results of ^{31}P, ^{183}W HMQC experiments, like signs (Figure 5). Inspection of the metal chemical shifts of **3b** ($\delta(^{183}W) = -3303$) and **4b** ($\delta(^{183}W) = -3221$) reveals that the different electronic properties of the ligands exert only very limited effects on the metal shielding.

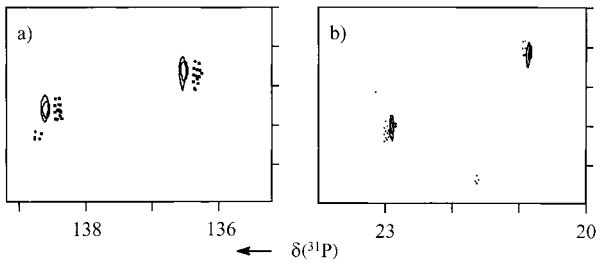


Figure 5. Phase-sensitive $^{31}P,^{183}W\{^{1}H\}$ HMQC spectra of [**3a**][Li(thf)$_x$] obtained with selective excitation of the phosphorus atoms in the 3-position (a) and 1-position (b) of the ring. The cross peaks are split by the active $^{2}J_{W,P3}/^{3}J_{W,P2}$ and the passive $^{2}J_{P,P}$ couplings in *F*2, and by the passive $^{3}J_{W,P2}/^{2}J_{W,P3}$ couplings in *F*1. The tilt of the cross peaks indicates like signs of all couplings $^{2}J_{P,P}$, $^{2}J_{W,P3}$, and $^{3}J_{W,P2}$.

Comparison of the NMR data of all the heterocycles studied reveals, in the case of the the lithium compounds [**3a**(**3b**)][Li(thf)$_n$], a relative deshielding of the oxygenated- and a strong shielding of the metalated-carbon atom ($\delta(^{13}C) = 107.9$) in comparison to the remaining compounds. These effects, together with the greatly reduced value of $^{2}J_{P,P}$, are in full agreement with a description of the canonical structure **A** (Scheme 3) for **3a**,**b** and presumably reflect the different π-electron distribution in the five-membered ring. The given description of the bonding in terms of superposition of the canonical structures shown in Scheme 3 is further in accord with the observed pattern of $^{1}J_{P,C}$ coupling constants between the phosphorus atoms and the endocyclic-silylated carbon atom and the *ipso*-carbon atoms of the Mes* substituents, respectively. The increased size of $^{1}J_{P,C}$ coupling to the phosphorus atoms at the 3-position of the rings in **3**–**6** adheres to the known trend that $^{1}J_{P,C}$ coupling involving formally pentavalent $\lambda^5\sigma^3$- and $\lambda^5\sigma^4$-phosphorus atoms is generally larger than that involving tervalent $\lambda^3\sigma^3$-phosphorus atoms.[20–22] This also agrees with the somewhat greater preference for canonical structures

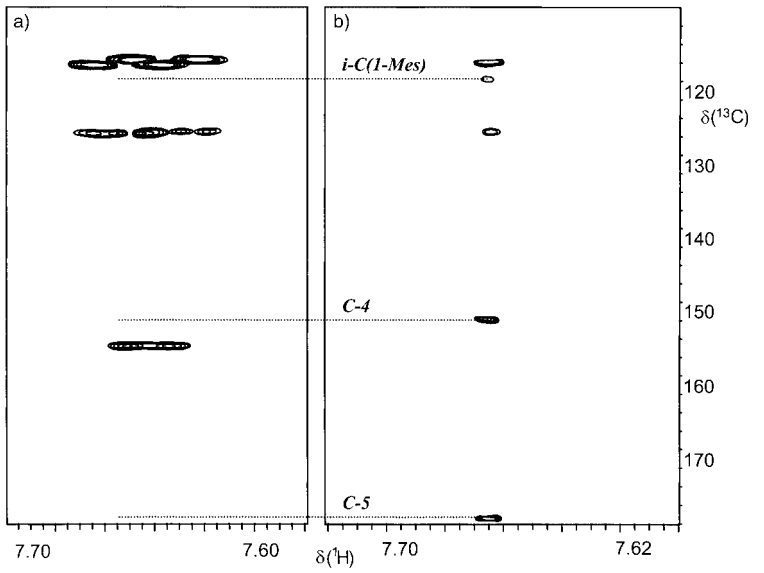


Figure 4. Expansions of gs-$^{1}H,^{13}C$-HMBC (left, defocusing delays of 60 ms for H,C coherence transfer) and ^{31}P-relayed gs-$^{1}H,^{13}C$-HSQC spectra (right, defocusing delays of 31 ms for H,P and of 5 ms for C,P coherence transfer) of **4b** at the chemical shift of the aromatic proton of the Mes* substituent at the P3 atom. The splitting of the cross peaks in the HMBC spectrum along the *F*2 direction are caused by $^{n}J_{P,H}$ and $^{n}J_{C,H}$ couplings, which were removed in the right spectrum by simultaneous decoupling of both heteronuclei. The cross peaks in the $^{1}H,^{13}C$ HMBC spectrum are attributable to correlations by $^{2,3}J_{C,H}$ connecting the hydrogen to the *ipso*-, *meta*-, and *para*-carbon atoms in the same ring. The additional cross peaks in the ^{31}P-relayed $^{1}H,^{13}C$-HSQC spectrum correspond to ^{31}P-relayed coherence transfers from the observed proton to the C4 and C5 carbon atoms of the central heterocycle, and to the *ipso*-C atom of the Mes* substituent at P1. The correlation signal to the C2 atom of the P_2C_3 heterocycle coincides with that of the H–C_{meta} correlation signal. In connection with the identification of the resonance signals of the C2 and C4 carbons from the $^{1}H,^{13}C$ HMBC spectrum (not shown), the displayed spectrum proves the assignment of the resonance of the carbenic C4 atom.

  0947-6539/02/0809-2192 $ 20.00+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 9

with higher formal valence at this atom (**A** and **B** in Scheme 3).

The signals of the formal carbenic carbon atoms in all compounds are considerably more shielded in comparison to reported values of genuine carbene complexes ($\delta(^{13}C) = 230-400$ for $R_2C{=}Cr(CO)_5$ and $\delta(^{13}C) = 180-360$ for $R_2C{=}W(CO)_5$,[20]) and appear even more shielded than those for complexes of Arduengo-type carbenes ($\delta(^{13}C) = 188$ (M = Cr), 179 (M = W) for $[M(CO)_5\{C(NMeCHCHNMe)\}]$.[23]) The failure to detect ^{183}W satellites for the carbenic resonances of **3a** and **4a** suggests that the $^1J_{W,C}$ coupling is not resolved (< 10 Hz) and is thus much smaller than in complexes of type $R_2C{=}W(CO)_5$ ($^1J_{W,C} = 70-110$[20]). In connection with the observed structural data, these effects may be interpreted in terms of low M–C bond orders and suggest that the coordinated phosphorus heterocycles are very weak π accceptors. Furthermore, the M–C bond can be essentially described in terms of a C → M dative interaction with negligible contributions from C ← M back donation.

Computational studies: To understand the formation of the five-membered diphosphole ring, quantum-chemical calculations were carried out[24] with a model complex (**8a**) built from 2-silyl-1,3-diphosphacyclobutane-2,4-diyl-2-ide and $[Cr(CO)_6]$ (Figure 6). Compound **8a** is obtained as a real minimum on the potential energy surface. The unsubstituted ring carbon atom is attached to one of the carbonyl carbon atoms of $[Cr(CO)_6]$. The intermediate **10a** is obtained via a low-lying transition state of structure **9a**, which is only 12 kcal mol^{-1} higher in energy than **8a**. The formation of transition state **9a** can be understood by two simultaneous movements of the nuclei: the ring of **8a** opens up along a C–P bond, which is adjacent to the carbon atom attacked previously, and at the same time the $Cr(CO)_5$ fragment shifts to the neighboring carbon atom, as shown by the single imaginary frequency obtained for this transition state. In the intermediate **10a** the ring has opened up completely. Compound **10a** is more stable (−40 kcal mol^{-1}, Table 1) than the initially formed complex **8a**.

Starting with **10a**, the product **12a** can be obtained via transition state **11a**, which is 10 kcal mol^{-1} lower in energy than the initial complex **8a** (and is 30 kcal mol^{-1} higher in energy than the intermediate **10a**). The imaginary mode computed for **11a** is clearly the ring-closing motion. The whole reaction pathway is shown in Scheme 4. The model compound **12a** of the observed product (**3a**), is more stable (−21 kcal mol^{-1}) than the initial complex **8a**. Thus it is considerably less stable than **10a**, contradicting the observation that the five-membered ring has in fact formed during the reaction sequence.

Table 1. Computed relative energies (with respect to **8**) for the model compounds **9**–**12** (cf. Figure 6).[24]

	9	10	11	12
a: R = H	12.0	−40.0	−10.0	−21.0
b: R = 2,6-dimethylphenyl	12.7	−22.9	8.9	−17.3
c: R = 2,6-di-*tert*-butylphenyl	–	−23.1	–	−19.1

It is very likely that, with the real substituents, the relative energies of the isomers will change. To model the effect of the substituting groups on the phosphorus atoms, the 2,6-dimethylphenyl moiety was used first. As shown in Table 1, neither the relative energy of the first transition state **9b** nor that of the product **12b** changed significantly in relation to the energy of the initially formed complex **8b**. However, the relative energies of **10b** and **11b** are considerably destabilized with respect to the simplest model system used here (hydrogen substituent on phosphorus). Nevertheless, the model compound calculated for the product **12b** is still less stable (5.6 kcal mol^{-1}) than **10b**. Minima were also calculated with the bulkier 2,6-di-*tert*-butylphenyl substituent at the phosphorus atoms (these calculations were carried out at the B3LYP/3-21G* level). The energy difference between **10c** and **12c** decreases slightly (4.0 kcal mol^{-1}) in comparison to that of **10b** and **12b**. Finally, an inspection of the optimized structures of **10c** and **12c**, in which the silyl group is replaced with the bulkier trimethylsilyl substituent, showed that in this case **12c** is more stable than **10c** by 2.9 kcal mol^{-1}.

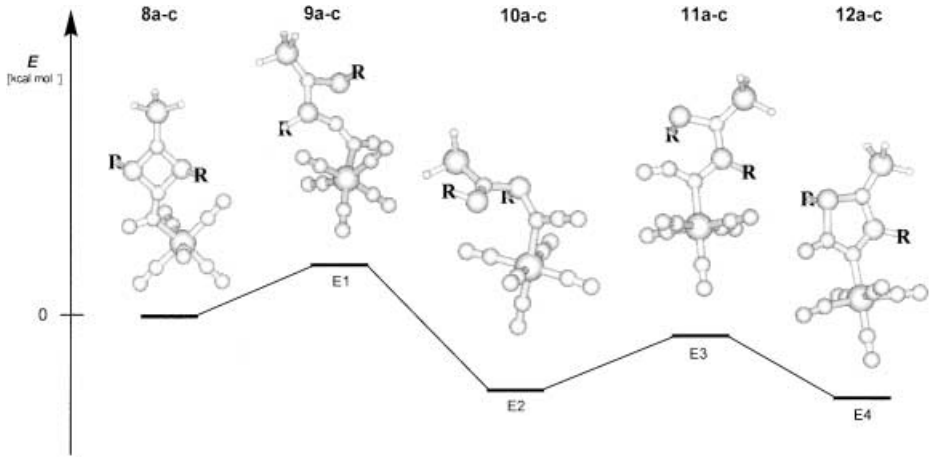
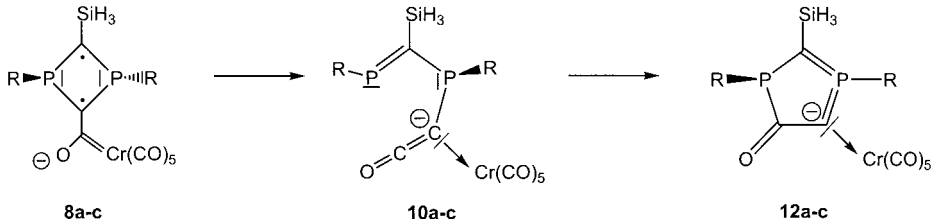


Figure 6. Energies of the compounds **8**–**12** from quantum-chemical calculations (see Table 1 for details).



Scheme 4. **a**: R = H; **b**: R = 2,6-dimethylphenyl; **c**: R = 2,6-di-*tert*-butylphenyl.

Conclusion

The ring expansion reaction of a 1,3-diphosphetane-2,4-diyl-2-ide, proceeding by CO insertion with metal hexacarbonyls to give the anionic complexes **3a**,**b** represents an unprecedented opportunity to access a novel type of diphosphorus heterocycle. The spectroscopic and structural features of the products suggest that these are best described in terms of heterocyclic ylide complexes whose coordinated carbon atom forms part of a bis(methylene)phosphorane moiety with a planar three-coordinate phosphorus atom. The transformation of **3a**,**b** into the neutral complexes **4**–**6** results in significant changes in both molecular structures and spectroscopic data which suggest development of a considerable degree of cyclic π-delocalization. The formation of a fully aromatic system with an ideal degree of electron delocalization and equalising of bond length is presumably prevented by the known preference of three-coordinate phosphorus centers to remain pyramidal, owing to the inability to allow isovalent orbital hybridization at phosphorus atoms. The long C–M bond indicates that the π acidity of the present heterocycles is presumably still lower than that of Arduengo-type carbenes, and highlights a similarity with complexes of classical phosphonium ylides.

Computational studies suggest that the ring expansion leading to **3a**, **b** proceeds by following an interesting sequence of ring-opening and -closure steps, and includes the rearrangement of an anionic ketenyl complex as a key intermediate. The detection of this product is presumably prevented by the accumulation of sterically overloaded substituents on the P–C–P triad.

The successful synthesis of the heterocycles described here stimulates further study of similar systems. A particularly interesting objective for further research is the design of rings featuring formal replacement of the phosphorus by nitrogen atoms. These compounds would represent species that are isomers of the imidazoline-2-ylidenes ("Arduengo-type" carbenes) **I**.

Experimental Section

General remarks: All reactions were carried out under dry argon. Solvents were dried by standard procedures.

NMR spectra were recored on a Bruker AMX 300 spectrometer (^{1}H: 300.1 MHz, ^{31}P: 121.5 MHz, ^{13}C: 75.4 MHz, ^{183}W: 12.5 MHz); chemical shifts were referenced to external TMS (^{1}H, ^{13}C), 85% H_3PO_4 (Θ = 40.480747 MHz, ^{31}P), aq. $[WO_4]^{2-}$ (Θ = 4.166388 MHz, ^{183}W). Positive signs denote shifts to lower frequencies, and coupling constants are given as absolute values. Gradient-selected (gs) two-dimensional ^{1}H NOESY, and ^{1}H,^{13}C or ^{1}H,^{31}P HMQC/HSQC experiments were obtained by using standard pulse sequences. Gradient-selected, ^{31}P relayed ^{1}H,^{13}C HSQC experiments were performed by using a pulse sequence obtained by modification of the original three-dimensional ^{1}H/^{13}C/^{31}P{^{29}Si} correlation schemes developed by Rinaldi et al.[19] by appropriate adjustment of the three NMR channels and gradient strengths to the nuclides ^{1}H, ^{31}P, ^{13}C and replacing the F2 evolution period by a fixed delay. Selective excitation of ^{31}P resonances was achieved by using rectangular pulses of sufficiently low power.[25] By using this set-up, the experiment corresponds to the sampling of a two-dimensional slice of a three-dimensional cube at a desired fixed ^{31}P chemical shift. Values of δ(^{183}W) were obtained from semi-selective, ^{31}P-detected ^{31}P,^{183}W{^{1}H}-HMQC[26] and ^{31}P-relayed ^{1}H,^{183}W-HSQC experiments using the same pulse sequence as described above. Relative signs of $^nJ_{W,P}$ couplings were determined from tilted cross peaks in ^{31}P,^{183}W HMQC spectra. Assignment of individual $J_{P,H}$ couplings was carried out from selectively decoupled ^{1}H{^{31}P} NMR spectra, and $J_{P,C}$ couplings were assigned by analysis of the splitting and intensity of correlation signals in suitable two-dimensional NMR spectra. Missing entries for some ^{13}C resonance signals arise from the fact that a secure signal assignment was, in these cases, prevented by severe signal overlap, or insufficient signal-to-noise ratios.

Mass spectra were recorded on a VG-Instruments VG 12–250 spectrometer.

Melting points were determined in sealed capillaries.

Lithium [1,3-bis-(2,4,6-tri-*tert*-butylphenyl)-2-trimethylsilyl-5-oxo-1,3-diphospholene-4-ylidene chromium pentacarbonyl] [**3a**][Li(thf)$_3$]: A suspension of [Cr(CO)$_6$] (0.5 mmol) in THF (10 mL) was added to a solution of [**1**][Li(thf)$_x$], which was prepared by reaction of Mes*PC(H)C(SiMe$_3$)PMes*[4] (325 mg, 0.5 mmol) in THF (10 mL) with lithium diisopropylamide (LDA; 0.5 mmol). The mixture was stirred until the metal carbonyl had dissolved completely. After two days, [**3a**][Li(thf)$_3$] crystallized from the reaction mixture. Yield: 330 mg, (76%); m.p. 143–145 °C; ^{1}H NMR (C_6D_6): δ = –0.10 (s; SiCH$_3$), 1.37 (s; *p*-*t*Bu(1-Mes*/3-Mes*)), 1.41 (s; *p*-*t*Bu(1-Mes*/3-Mes*)), 1.47 (d, $^5J_{P1,H}$ = 0.6 Hz; *o*-*t*Bu(1-Mes*)), 1.61 (dd, $^5J_{P3,H}$ = 1.1 Hz, $^7J_{P1,H}$ = 0.8 Hz; *o*-*t*Bu(3-Mes*)), 7.69 (d, $^4J_{P1,H}$ = 2.0 Hz; *m*-H(1-Mes*)), 7.82 (d, $^4J_{P3,H}$ = 3.9 Hz; *m*-H(3-Mes*)); ^{31}P{^{1}H} NMR (C_6D_6): δ = 31.2 (d, $^2J_{P,P}$ = 327 Hz; P-1), 109.4 (d, $^2J_{P,P}$ = 327 Hz; P-3).

Lithium [1,3-bis-(2,4,6-tri-*tert*-butylphenyl)-2-trimethylsilyl-5-oxo-1,3-diphospholene-4-ylidene tungsten pentacarbonyl] [**3b**][Li(thf)$_x$]: A suspension of [W(CO)$_6$] (1 mmol) in THF (15 mL) was added to a solution of [**1**][Li(thf)$_x$], prepared by reaction of Mes*PC(H)C(SiMe$_3$)PMes*[4] (650 mg (1 mmol)) in THF (10 mL) with LDA (2 mmol). The mixture was stirred until the metal carbonyl had dissolved completely. After two days, [**3b**][Li(thf)$_x$] crystallized from the reaction mixture. Yield: 390 mg, 60%; ^{1}H NMR (C_6D_6): δ = –0.24 (s; SiCH$_3$), 1.25 (s; *p*-*t*Bu(1-Mes*/3-Mes*)), 1.29 (s; *p*-*t*Bu(1-Mes*/3-Mes*)), 1.82 (br; *o*-*t*Bu(1-Mes*)), 1.93 (br; *o*-*t*Bu(3-Mes*)), 7.56 (d, $^4J_{P3,H}$ = 2.4 Hz; *m*-H(1-Mes*)), 7.69 (dd, $^4J_{P3,H}$ = 4.0 Hz, $^6J_{P1,H}$ = 0.5 Hz; *m*-H(3-Mes*)); ^{13}C{^{1}H} NMR (C_6D_6): δ = 1.8 (dd, $^3J_{P,C}$ = 3.2 Hz; 1.3 Hz, SiMe$_3$), 107.9 (d, $^1J_{P3,C}$ = 45.0 Hz; C-4), 126.6 (dd, $^1J_{P1,C}$ = 18.3 Hz, $^1J_{P3,C}$ = 39.7 Hz; C-2), 203.0 (dd, $^3J_{P3,C}$ = 2.3 Hz, $^1J_{W,C}$ = 125.9 Hz; CO_{eq}), 203.3 (dd, $^1J_{P1,C}$ = 38.5 Hz, $^2J_{P3,C}$ = 9.5 Hz; C-5), 203.7 (d, $^1J_{W,C}$ = 1.9 Hz; CO_{ax}); 1-Mes*: 31.1 (s; *p*-*C*CH$_3$), 34.1 (d, $^4J_{P1,C}$ = 2.7 Hz; *o*-*C*CH$_3$), 35.1 (s; *p*-*C*CH$_3$), 39.6 (d, $^3J_{P1,C}$ = 3.8 Hz; *o*-*C*CH$_3$), 123.6 (d, $^1J_{P1,C}$ = 8.4 Hz; C_{ipso}), 124.1 (dd, $^3J_{P1,C}$ = 19.5 Hz, $^5J_{P3,C}$ = 3.4 Hz; C_{meta}), 154.0 (d, $^4J_{P1,C}$ = 2.7 Hz; C_{para}), 159.1 (dd, $^2J_{P1,C}$ = 10.7 Hz, $^4J_{P3,C}$ = 3.4 Hz; C_{ortho}); 3-Mes*: 30.8 (s; *p*-*C*CH$_3$), 34.9 (d, $^4J_{P3,C}$ = 1.5 Hz; *o*-*C*CH$_3$), 35.4 (s; *p*-*C*CH$_3$), 40.9 (d, $^3J_{P3,C}$ = 2.3 Hz; *o*-*C*CH$_3$), 121.0 (dd, $^1J_{P3,C}$ = 59.5 Hz, $^3J_{P1,C}$ = 2.7 Hz; C_{ipso}), 125.9 (d, $^3J_{P3,C}$ = 11.4 Hz; C_{meta}), 152.1 (d, $^4J_{P3,C}$ = 3.1 Hz; C_{para}), 156.0 (dd, $^2J_{P3,C}$ = 7.2 Hz, $^4J_{P1,C}$ = 5.7 Hz; C_{ortho}); ^{31}P{^{1}H} NMR (CH_2Cl_2): δ = 24.9 (d, $^2J_{P,P}$ = 258 Hz, $^3J_{WP}$ = 11.9 Hz; P-1), 135.2 (d, $^2J_{P,P}$ = 258 Hz, $^2J_{WP}$ = 25.2 Hz; P3).

1,3-Bis-(2,4,6-tri-*tert*-butylphenyl)-2-trimethylsilyl-5-methoxy-1,3-diphospholene-4-ylidene chromium pentacarbonyl (4a), 1,3-bis-(2,4,6-tri-*tert*-butylphenyl)-2-trimethylsilyl-5-trimethylsilyloxy-1,3-diphospholene-4-ylidene chromium pentacarbonyl (5), and 1,3-bis-(2,4,6-tri-*tert*-butylphenyl)-2-trimethylsilyl-5-hydroxy-1,3-diphospholene-4-ylidene chromium pentacarbonyl (6): A solution of either Me$_3$SiCl (0.4 mmol) in THF (10 mL), [Me$_3$O][BF$_4$] (0.4 mmol) in CH_2Cl_2 (2 mL), or pyridinium hydrochloride (0.3 mL of a 1 mol L^{-1} solution in THF) in THF (3 mL) was added at 25 °C to a solution of **3a** (260 mg, 0.3 mmol) in THF (10 mL). The mixture was stirred for one hour and any volatiles were removed in vacuo. The residue was dissolved in *n*-pentane (10 mL) and filtered to remove precipitated LiX. Storing the redish solution at 0 °C yielded the products **4a**, **5**, **6** as orange crystals.

4a: Yield 230 mg, 86%; m.p. 143–145 °C; ^{1}H NMR (C_6D_6): δ = –0.29 (s; SiCH$_3$), 1.23 (s; *p*-*t*Bu(1-Mes*/3-Mes*)), 1.24 (s; *p*-*t*Bu(1-Mes*/3-Mes*)), 1.47 (d, $^5J_{P1,H}$ = 0.6 Hz; *o*-*t*Bu(1-Mes*)), 1.61 (dd, $^5J_{P3,H}$ = 1.1 Hz, $^7J_{P1,H}$ = 0.8 Hz; *o*-*t*Bu(3-Mes*)), 3.97 (d, $^4J_{P1,H}$ = 0.8 Hz; OMe), 7.57 (dd, $^4J_{P1,H}$ = 3.6 Hz, $^6J_{P3,H}$ = 0.5 Hz; *m*-H(1-Mes*)), 7.72 (dd, $^4J_{P3,H}$ = 4.6 Hz, $^6J_{P1,H}$ = 0.7 Hz; *m*-H(3-Mes*)); ^{13}C{^{1}H} NMR (C_6D_6): δ = 1.8 (d, $^3J_{P,C}$ = 2.5 Hz, 3.3 Hz; SiMe$_3$), 62.7 (dd, $J_{P,C}$ = 3.8 Hz, 5.3 Hz; OCH$_3$), 126.6 (dd, $^1J_{P1,C}$ = 13.0 Hz, $^1J_{P3,C}$ = 21.4 Hz; C-2), 162.9 (d, $^1J_{P3,C}$ = 2.7 Hz; C-4), 178.0 (dd,

  0947-6539/02/0809-2194 $ 20.00+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 9

$^1J_{P1,C}=41.6$ Hz, $^2J_{P3,C}=28.2$ Hz; C-5), 220.3 (dd, $^3J_{P3,C}=4.6$ Hz, $^4J_{P1,C}=1.0$ Hz; CO_{eq}), 224.2 (s; CO_{ax}); 1-Mes*: 31.3 (s; *p*-CCH_3), 34.1 (t, $^4J_{P1,C}=1.3$ Hz, $^7J_{P3,C}=1.3$ Hz; *o*-CCH_3), 35.4 (s; *p*-CCH_3), 39.8 (d, $^3J_{P1,C}=3.4$ Hz; *o*-CCH_3), 120.5 (dd, $^1J_{P1,C}=15.1$ Hz, $^3J_{P3,C}=10.9$ Hz; C_{ipso}), 124.7 (d, $^3J_{P1,C}=9.9$ Hz; C_{meta}), 155.7 (d, $^4J_{P1,C}=3.4$ Hz; C_{para}), 159.4 (dd, $^2J_{P1,C}=9.4$, $^4J_{P3,C}=5.2$ Hz; C_{ortho}); 3-Mes*: 31.3 (s; *p*-CCH_3), 35.5 (d, $^4J_{P3,C}=1.6$ Hz; *o*-CCH_3), 35.4 (s; *p*-CCH_3), 41.1 (d, $^3J_{P3,C}=2.3$ Hz; *o*-CCH_3), 117.6 (d, $^1J_{P3,C}=54.7$ Hz; C_{ipso}), 126.9 (d, $^3J_{P3,C}=12.2$ Hz; C_{meta}), 155.3 (d, $^4J_{P3,C}=3.1$ Hz; C_{para}), 157.5 (dd, $J_{P,C}=7.8$ Hz, 7.0 Hz; C_{ortho}); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta=31.2$ (d, $^2J_{P,P}=327$ Hz; P-1), 109.4 (d, $^2J_{P,P}=327$ Hz; P-3); MS (70 eV, FAB): *m/z* (%): 800 (4) $[M-3CO]^+$, 772 (23) $[M-4CO]^+$, 744 (13) $[M^+-5CO]^+$, 693 (100) $[MH-Cr(CO)_5]^+$.

5: Yield: 140 mg, 49%; m.p. 226–228 °C; ^1H NMR (THF-d_8): $\delta=-0.25$ (s; $SiCH_3$), −0.58 (s; $SiCH_3$), 1.22 (s; *p*-*t*Bu(1-Mes*/3-Mes*)), 1.23 (s; *p*-*t*Bu(1-Mes*/3-Mes*)), 1.35 (s; *o*-*t*Bu(1-Mes*)), 1.46 (s; *o*-*t*Bu(3-Mes*)), 7.51 (d, $^4J_{P1,H}=4.4$ Hz; *m*-H(1-Mes*)), 7.61 (d, $^4J_{P3,H}=3.5$ Hz; *m*-H(3-Mes*)); $^{13}C\{^1H\}$ NMR (THF-d_8): $\delta=-0.8$ (s; $OSiMe_3$), −0.5 (s; $CSiMe_3$), 129.7 (dd, $^1J_{P1,C}=4.2$ Hz, $^1J_{P3,C}=30.5$ Hz; C-2), 173.8 (dd, $^1J_{P1,C}=28.6$ Hz, $^2J_{P3,C}=2.1$ Hz; C-5), 218.0 (dd, $^3J_{P3,C}=4.2$ Hz, $^4J_{P3,C}=1.2$ Hz; CO_{eq}), 221.8 (s; CO_{ax}); 1-Mes*: 28.8 (s; *p*-CCH_3), 31.6 (d, $^4J_{P1,C}=1.5$ Hz; *o*-CCH_3), 33.5 (s; *p*-CCH_3), 37.7 (d, $^3J_{P1,C}=3.8$ Hz; *o*-CCH_3), 122.5 (d, $^3J_{P1,C}=10.0$ Hz; C_{meta}), 153.7 (d, $^4J_{P1,C}=3.1$ Hz; C_{para}), 158.2 (dd, $^2J_{P1,C}=10.3$, $^4J_{P3,C}=5.0$ Hz; C_{ortho}); 3-Mes*: 28.7 (s; *p*-CCH_3), 32.9 (d, $^4J_{P3,C}=1.9$ Hz; *o*-CCH_3), 33.5 (s; *p*-CCH_3), 38.9 (d, $^3J_{P3,C}=2.3$ Hz; *o*-CCH_3), 115.7 (dd, $^1J_{P3,C}=56.1$ Hz, $^3J_{P1,C}=1.5$ Hz; C_{ipso}), 124.6 (d, $^3J_{P3,C}=12.6$ Hz; C_{meta}), 153.4 (d, $^4J_{P3,C}=3.4$ Hz; C_{para}), 155.5 (dd, $^2J_{P3,C}=8.4$ Hz, $^4J_{P1,C}=6.7$ Hz; C_{ortho}); $^{31}P\{^1H\}$ NMR (CH_2Cl_2): $\delta=30.5$ (d, $^2J_{P,P}=322$ Hz; P-1), 118.5 (d, $^2J_{P,P}=322$ Hz; P-3); MS (70 eV, FAB): *m/z* (%): 830 (10) $[M-4CO]^+$, 749 (15) $[M-Cr(CO)_5]^+$, 669 (27) $[M-CO-Mes^*]^+$, 613 (100) $[M-3\,CO-Mes^*]^+$, 433 (49) $[M-Cr(CO)_5-Mes^*-Tms]^+$.

6: Yield: 190 mg, 73%; m.p. 160–162 °C; ^1H NMR (C_6D_6): $\delta=0.11$ (s; $SiCH_3$), 1.19 (s; *p*-*t*Bu(1-Mes*/3-Mes*)), 1.22 (s; *p*-*t*Bu(1-Mes*/3-Mes*)), 1.48 (s; *o*-*t*Bu(1-Mes*/3-Mes*)), 1.55 (s; *o*-*t*Bu(1-Mes*/3-Mes*)), 7.53 (d, $^4J_{P1,H}=3.5$ Hz; *m*-H(1-Mes*)), 7.64 (d, $^4J_{P3,H}=4.2$ Hz; *m*-H(3-Mes*)), 7.7 (br d, $J_{PH}=22.1$ Hz; OH); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta=1.7$ (s; $SiMe_3$), 189.9 (dd, $^1J_{P1,C}=23.6$ Hz, $^2J_{P3,C}=9.2$ Hz; C-5), 220.0 (d, $^3J_{P3,C}=3.8$ Hz; CO_{eq}), 223.6 (s; CO_{ax}); 1-Mes*: 31.4 (s; *p*-CCH_3), 32.1 (s; *o*-CCH_3), 35.2 (s; *p*-CCH_3), 39.9 (d, $^3J_{P1,C}=4.2$ Hz; *o*-CCH_3), 124.1 (d, $^3J_{P1,C}=11.5$ Hz; C_{meta}), 156.1 (d, $^4J_{P1,C}=3.4$ Hz; C_{para}), 160.9 (dd, $^2J_{P1,C}=10.3$, $^4J_{P3,C}=4.4$ Hz; C_{ortho}); 3-Mes*: 31.1 (s; *p*-CCH_3), 34.1 (br s; *o*-CCH_3), 35.6 (s; *p*-CCH_3), 41.0 (d, $^3J_{P3,C}=2.3$ Hz; *o*-CCH_3), 118.6 (dd, $^1J_{P3,C}=47.8$ Hz, $^3J_{P1,C}=1.7$ Hz; C_{ipso}), 126.7 (d, $^3J_{P3,C}=12.6$ Hz; C_{meta}), 155.2 (d, $^4J_{P3,C}=3.0$ Hz; C_{para}), 157.8 (dd, $J_{P,C}=8.4$ Hz, 6.5 Hz; C_{ortho}); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta=17.8$ (d, $^2J_{P,P}=335$ Hz; P-1), 117.0 (d, $^2J_{P,P}=335$ Hz; P-3); MS (70 eV, FAB): *m/z* (%): 870 (1) $[M]^+$, 842 (1.5) $[M-CO]^+$, 786 (2) $[M-3CO]^+$, 758 (10) $[M-4CO]^+$, 730 (46) $[M-5CO)^+$, 485 (100) $[M-5CO-Mes^*]^+$.

1,3-Bis-(2,4,6-tri-*tert*-butylphenyl)-2-trimethylsilyl-5-methoxyimidazole-4-ylidene tungsten pentacarbonyl (4b): A solution of $[Me_3O][BF_4]$ (0.5 mmol) in CH_2Cl_2 (10 mL) was added to a solution of **3b** (504 mg, 0.5 mmol) in CH_2Cl_2 (10 mL) at 25 °C. The mixture was stirred for one hour and any volatiles were removed in vacuo. The residue was dissolved in *n*-pentane (15 mL) and filtered to remove precipitated LiX. Storing the brown solution at 0 °C yielded **4b** as yellow crystals. Yield: 447 mg, 88%; ^1H NMR (C_6D_6): $\delta=-0.34$ (s; $SiCH_3$), 1.19 (s; *p*-*t*Bu(1-Mes*/3-Mes*)), 1.42 (d, $^5J_{P1,H}=0.7$ Hz; *o*-*t*Bu(1-Mes*)), 1.55 (dd, $^5J_{P3,H}=1.4$ Hz, $^7J_{P1,H}=0.7$ Hz; *o*-*t*Bu(3-Mes*)), 3.94 (d, $^4J_{P1,H}=1.0$ Hz; OMe), 7.52 (dd, $^4J_{P1,H}=3.8$ Hz, $^6J_{P3,H}=0.5$ Hz; *m*-H(1-Mes*)), 7.66 (dd, $^4J_{P3,H}=4.7$ Hz, $^6J_{P1,H}=0.8$ Hz; *m*-H(3-Mes*)); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta=1.7$ (t, $^3J_{P,C}=2.8$ Hz; $SiMe_3$), 62.7 (dd, $J_{P,C}=3.6$ Hz, 5.5 Hz; OCH_3), 126.1 (dd, $^1J_{P1,C}=11.6$ Hz, $^1J_{P3,C}=23.2$ Hz; C-2), 152.3 (d, $^1J_{P3,C}=28.5$ Hz; C-4), 179.1 (dd, $^1J_{P1,C}=42.0$ Hz, $^2J_{P3,C}=30.1$ Hz; C-5), 201.0 (dd, $^3J_{P3,C}=4.2$ Hz, $^1J_{W,C}=125.7$ Hz; CO_{eq}), 202.6 (d, $^1J_{W,C}=134.4$ Hz; CO_{ax}); 1-Mes*: 31.2 (s; *p*-CCH_3), 34.2 (d, $^4J_{P1,C}=1.6$ Hz; *o*-CCH_3), 35.5 (s; *p*-CCH_3), 40.0 (d, $^3J_{P1,C}=3.6$ Hz; *o*-CCH_3), 119.9 (dd, $^1J_{P1,C}=15.9$ Hz, $^3J_{P3,C}=9.5$ Hz; C_{ipso}), 124.6 (d, $^3J_{P1,C}=10.8$ Hz; C_{meta}), 155.9 (d, $^4J_{P1,C}=2.9$ Hz; C_{para}), 159.7 (dd, $^2J_{P1,C}=9.4$, $^4J_{P3,C}=4.8$ Hz; C_{ortho}); 3-Mes*: 31.1 (s; *p*-CCH_3), 35.5 (d, $^4J_{P3,C}=1.5$ Hz; *o*-CCH_3), 35.5 (s; *p*-CCH_3), 41.2 (d; $^3J_{P3,C}=2.2$ Hz; *o*-CCH_3), 117.4 (d, $^1J_{P3,C}=56.9$ Hz; C_{ipso}), 127.0 (d, $^3J_{P3,C}=12.6$ Hz; C_{meta}), 155.3 (d, $^4J_{P3,C}=3.2$ Hz; C_{para}), 157.7 (dd,

Table 2. Crystallographic data, structure solution and refinement of [**3a**][Li(thf)$_3$], **4a**,**b**, and **5**.

	[**3a**][Li(thf)$_3$]	**4a**	**4b**	**5**
formula	$C_{59}H_{91}CrLiO_9P_2Si\cdot 2\,THF$	$C_{48}H_{70}CrO_6P_2Si$	$C_{48}H_{70}O_6P_2SiW$	$C_{50}H_{76}CrO_6P_2Si_2\cdot$ cyclopentane
M_r	1237.50	885.07	1016.92	1013.36
crystal size [mm]	0.35 × 0.25 × 0.13	0.30 × 0.20 × 0.05	0.50 × 0.30 × 0.20	0.35 × 0.25 × 0.10
color	red	orange	yellow	orange
crystal system	monoclinic	orthorhombic	orthorhombic	monoclinic
space group	$P2_1/c$ (no.14)	*Pbca* (no.61)	*Pbca* (no.61)	$P2_1/n$ (no.14)
a [Å]	22.772(2)	11.8335(2)	11.8960(1)	11.3537(7)
b [Å]	10.509(10)	21.2361(4)	21.2508(3)	26.1575(11)
c [Å]	31.821(3)	38.7891(7)	38.8353(5)	19.4068(11)
β [°]	109.54(1)			99.282(2)
V [Å^3]	7176.5(11)	9747.6(3)	9817.5(2)	5688.1(5)
Z	4	8	8	4
ρ [g cm^{-1}]	1.145	1.206	1.376	1.183
μ [mm^{-1}]	2.312	0.369	2.487	0.345
F(000)	2672	3792	4192	2184
diffractometer	Nonius Mach 3	Nonius Kappa CCD	Nonius Kappa CCD	Nonius Kappa CCD
radiation	$Cu_{K\alpha}$	$Mo_{K\alpha}$	$Mo_{K\alpha}$	$Mo_{K\alpha}$
λ [Å]	1.54178	0.71073	0.71073	0.71073
T [K]	200(2)	123(2)	123(2)	123(2)
Θ_{max} [°]	67.86	25.00	25.00	25.00
index range	$-27\le h\le 0$	$-14\le h\le 14$	$-14\le h\le 14$	$-13\le h\le 13$
	$-12\le k\le 0$	$-25\le k\le 25$	$-25\le k\le 23$	$-28\le k\le 29$
	$-36\le l\le 38$	$-46\le l\le 46$	$-46\le l\le 24$	$-23\le l\le 23$
reflections measured	13374	103495	34500	43137
unique reflections	13024	8549	8399	9705
observed reflections [$I>2\sigma(I)$]	10269	5877	6164	6213
R_{int}	0.057	0.089	0.053	0.072
parameters/restraints	879/1369	523/0	523/0	595/68
R [$I>2\sigma(I)$]	0.062	0.037	0.028	0.046
*wR*2 (all data)	0.184	0.089	0.060	0.129
largest diff. peak and hole [e$^-$ Å^3]	0.742/−0.528	0.307/−0.417	1.157/−0.803	0.547/−0.461
Goof on F^2	1.02	0.96	0.94	0.96

$^2J_{P3,C} = 7.1$ Hz, $^4J_{P1,C} = 7.1$ Hz; C_{ortho}); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 29.4$ (d, $^2J_{P,P} = 320$ Hz, $^3J_{WP} = 13.8$ Hz, P-1), 112.2 (d, $^2J_{P,P} = 320$ Hz, $^2J_{WP} = 15.2$ Hz, P-3).

Crystal structure determinations of compounds 3a – 5: The structures were solved by direct methods (SHELXS-97[27a]). The non-hydrogen atoms were refined anisotropically, H atoms were refined by using a riding model (full-matrix least-squares refinement on F^2(SHELXL-93[27b](**3a**), SHELXL-97[27c](**4a**,**b**, **5**))). Details of data collection and refinement are given in Table 2. For **3a**, extinction and empirical absorption corrections (min./max. transmission = 0.589/0.937) were applied. The *t*Bu groups and the two THF molecules are disordered. An empirical absorption correction was applied for **4b** (min./max. transmission = 0.3758/0.4403).

CCDC-116958 (**3a**), CCDC-143139 (**4a**), CCDC-72434 (**4b**), and CCDC-116959 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft (SFB 334) and the Fonds der Chemischen Industrie. Extracts were presented at the International Conference on Phosphorus Chemistry, Sendai, 31.7 – 4.8. 2001.

[1] T. Kato, H. Gornitzka, A. Baceiredo, A. Savin, G. Bertrand, *J. Am. Chem. Soc.* **2000**, *122*, 998 – 999, and references therein.
[2] A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361.
[3] D. Bourissou, O. Guerret, F. P. Gabbai, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39 – 91, and references therein.
[4] W. W. Schoeller, D. Eisner, S. Grigoleit, A. B. Rozhenko, A. Alijah, *J. Am. Chem. Soc.* **2000**, *122*, 10115 – 10120; W. W. Schoeller, A. B. Rozhenko, A. Alijah, *J. Organomet. Chem.* **2001**, *617*, 435 – 443.
[5] L. Nyulászi, D. Szieberth, J. Reffy, T. Veszprémi, *J. Mol. Struct. THEOCHEM* **1998**, *453*, 91 – 95.
[6] E. O. Fischer, R. Restmeier, K. Ackermann, *Z. Naturforsch.* **1983**, *38b*, 582.
[7] E. O. Fischer, F. R. Kreißl, C. G. Kreiter, E. W. Meineke, *Chem. Ber.* **1972**, *105*, 2558 – 2564; E. O. Fischer, R. Restmeier, K. Ackermann, *Angew. Chem.* **1983**, *93*, 419 – 420; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 411.
[8] E. Niecke, A. Fuchs, M. Nieger, O. Schmidt, W. W. Schoeller, *Angew. Chem.* **1999**, *111*, 3216 – 3219; *Angew. Chem. Int. Ed.* **1999**, *38*, 3031 – 3034.
[9] Phosphametallacyclobutenes that may be considered as Schrock-type phosphanylcarbene complexes are known: a) G. M. Jamison, R. S. Saunders, D. R. Wheeler, M. D. McClain, D. A. Loy, *Organometallics* **1996**, *15*, 16 – 18; b) G. M. Jamison, R. S. Saunders, D. R. Wheeler, T. M. Alam, M. D. McClain, D. A. Loy, *Organometallics* **1996**, *15*, 3244 – 3246.
[10] E. Niecke, A. Fuchs, M. Nieger, *Angew. Chem.* **1999**, *111*, 3213 – 3216; *Angew. Chem. Int. Ed.* **1999**, *38*, 3028 – 3031.
[11] W. C. Kaska, K. A. Ostoja Starzewski, in "*Ylides and Imines of Phosphorus*" (Ed.: A. W. Johnson), Wiley, New York, **1993**, 485 ff.
[12] ^{31}P NMR data: $\delta = 43.6$ (dd, $^2J(P,H) = 44.5$ Hz, $^2J(P,P) = 297.5$ Hz), 91.8 (dd, $^2J(P,H) = 29.3$ Hz, $^2J(P,H) = 297.5$ Hz).
[13] B. F. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, in "*International Tables for Crystallography*", *Vol. C* (Ed.: A. J. C. Wilson), Kluwer Academic Publishers, Dordrecht, **1992**, 685 ff. and 707 ff.
[14] Result of a search for compounds with the structural fragment $>C{=}Cr(CO)_5$ in the CCSD data base.
[15] E. O. Fischer, D. Wittmann, D. Himmelreich, D. Neugebauer, *Angew. Chem.* **1982**, *94*, 451 – 452; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 1036.
[16] F. Rosche, G. Heckmann, B. Neumüller, E. Fluck, *Z. Anorg. Allg. Chem.* **1996**, *622*, 642.
[17] C. W. Bird, *Tetrahedron* **1985**, *41*, 1409 – 1414.
[18] G. N. Cloke, P. B. Hitchcock, P. Hunnable, J. F. Nixon, L. Nyulàszi, E. Niecke, V. Thelen, *Angew. Chem.* **1998**, *110*, 1139 – 1142; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 1083 – 1086.
[19] a) T. Saito, R. E. Medsker, H. J. Harwood, P. L. Rinaldi, *J. Magn. Reson. Ser. A* **1996**, *120*, 125; b) M. Chai, T. Saito, Z. Pi, C. Tessier, P. L. Rinaldi, *Macromolecules* **1997**, *30*, 1240.
[20] B. E. Mann in "*Multinuclear NMR*" (Ed.: J. Mason), Plenum Press, New York, **1987**, 293.
[21] S. Berger, S. Braun, H.-O Kalinowski in *NMR-Spektroskopie von Nichtmetallen*, *Vol. 3*, Thieme, Stuttgart, **1993**, 86 ff.
[22] V. M. S. Gil, W. von Philipsborn, *Magn. Reson. Chem.* **1989**, *27*, 409.
[23] K. Öfele, W. A. Herrmann, D. Mihalios, M. Elison, E. Herdtweck, W. Scherer, J. Mink, *J. Organomet. Chem.* **1993**, *459*, 177 – 184.
[24] All computational calculations were carried out using the G98 suite of programs. Preliminary calculations were carried out at the B3LYP/3 – 21G* level. The optimization of the starting material, intermediate, and product, as well as the optimization of the transition state structures, was followed by calculation of the second derivatives to ensure that the structure obtained is a real minimum (all harmonic frequencies positive), or a first order saddle point (the structure has a single imaginary frequency). Further optimizations were carried out subsequently, at the B3LYP/6 – 31G*, starting from the geometries optimised at the lower level and reading in the calculated second derivatives. For the smallest model systems investigated (see text) second derivatives were again calculated at the B3lYP/6 – 31G* level. For those systems where the phosphorus was substituted by 2,6-dimethylphenyl groups, B3LYP/6 – 31 + G*//B3LYP/6 – 31G* calculations were carried out as well, since for anions the use of diffuse functions is usually important to achieve a proper description. To calculate the Gibbs free energies at 298 K the B3LYP/3 – 21G* (and when available the B3LYP/6 – 31G*), second derivatives were used. There was no significant difference between the relative energies and the relative Gibbs free energies of **8** – **12**.
[25] Further experimental details, as well as the pulse sequence, are available upon request from one of the authors (D. G.).
[26] D. Gudat, *Ann. Rep. NMR Spectrosc.* **1999**, *38*, 139.
[27] a) G. M. Sheldrick, SHELXS-97, *Acta Crystallogr.* **1990**, *A46*, 467 – 473; b) G. M. Sheldrick, SHELXL-93, Universität Göttingen, **1993**; c) G. M. Sheldrick, SHELXL-97, Universität Göttingen, **1997**.

Received: November 8, 2001 [F3671]

