A Mössbauer spectrum of a powder sample was recorded with a conventional spectrometer in the constant-acceleration mode. Isomer shifts are relative to α-Fe at room temperature. The spectrum was analyzed by a least-squares fit with a Lorentzian line shape. The Mössbauer spectrum of **1** (Figure 4) at 280 K exhibits an asymmetric doublet because of relaxation effects. The Mössbauer parameters ($\delta = 0.35\ \mathrm{mm\,s^{-1}}$ and $\Delta E_Q = 0.95\ \mathrm{mm\,s^{-1}}$) compare well with those of other high-spin iron(III) porphyrins, whereas the quadrupole splitting is considerably smaller than those of iron(III) porphyrin complexes which exhibit a substantial $S = 3/2$ admixture.[13–15, 19]

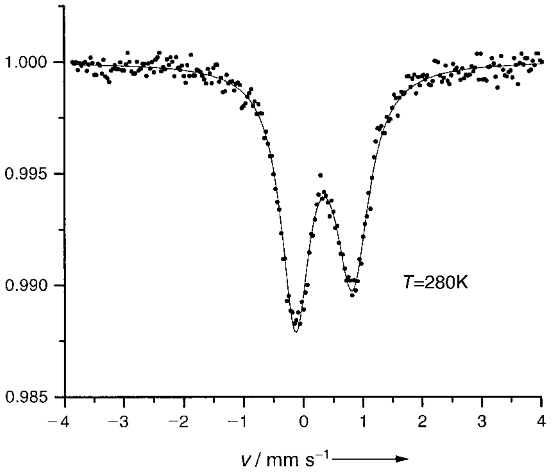

Figure 4. Mössbauer spectrum of a powder sample of **1** at 280 K in a field of 10 mT applied perpendicular to the γ beam. Two single lines of Lorentzian shape were used to fit the asymmetry of the spectrum, which is caused by relaxation effects: $\delta = 0.35\ \mathrm{mm\,s^{-1}}$, $\Delta E_Q = 0.95\ \mathrm{mm\,s^{-1}}$, $\Gamma_1 = 0.68\ \mathrm{mm\,s^{-1}}$, and $\Gamma_2 = 0.57\ \mathrm{mm\,s^{-1}}$. y = relative transmission, v = velocity.

In conclusion, a significantly smaller quantum-mechanical $S = 3/2$ spin admixture is present in the $[\mathrm{Fe^{III}Cl(oetpp)}]$ complex prepared by us (4–10%), as compared to that in the [FeCl(oetpp)] complex prepared by Cheng et al. (ca. 40%),[849] despite similar ring deformations in both complexes in solution and in the solid state.

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[17] a) Crystal data for **1**: $\mathrm{C_{60}H_{60}N_4ClFe}$, $M_r = 928.5$, monoclinic, space group $C2/c$, $a = 17.737(5)$, $b = 24.456(7)$, $c = 15.588(4)$ Å, $\beta = 111.24(2)^\circ$, $V = 6302$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 0.978\ \mathrm{g\,cm^{-3}}$, $\lambda(\mathrm{Mo_{K\alpha}}) = 0.7107$ Å, 6791 reflections ($2 < \theta < 26^\circ$) were collected at 20°C on a dark blue crystal of dimensions 0.35 × 0.30 × 0.25 mm. Semi-empirical absorption corrections were applied. A total of 3537 reflections with $I > 3\sigma(I)$ were used in the refinements; 299 refined parameters, $R = 0.073$, $R_w = 0.120$, GOF 1.036, final residual electron density 0.13 Å^3; b) Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-118960. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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Transition Metal Induced Pentamerization of a Phosphaalkyne**

Peter Kramkowski and Manfred Scheer*

Dedicated to Professor Manfred Regitz
on the occasion of his 65th birthday

The chemistry of the phosphaalkynes has been intensively investigated over the past 15 years in their various aspects of organoelement chemistry[1] and coordination chemistry.[2] The basis for this immense development was the first synthesis of kinetically stabilized $t\mathrm{BuC{\equiv}P}$ by G. Becker in 1981[3, 4] and the improved preparation by M. Regitz and G. Becker.[5] Most of the studies into the reactivity of phosphaalkynes have been carried out on this compound, whereas the supermesitylphosphaalkyne $\mathrm{Mes^*C{\equiv}P}$ ($\mathrm{Mes^*} = 2,4,6\text{-}t\mathrm{Bu_3C_6H_2}$) and the

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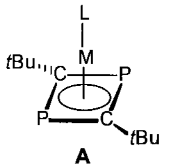
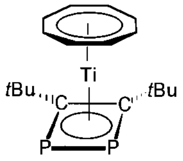
adamantyl-phosphaalkyne $AdC\equiv P$ ($Ad = C_{10}H_{15}$) have only been rarely included in such investigations. Recently Regitz and co-workers were able to synthesize mesityl-phosphaalkyne $MesC\equiv P$ ($Mes = 2,4,6\text{-}Me_3C_6H_2$) in preparatively useful quantities.[6]

A central aspect of the investigations on the reactivity of phosphaalkynes in transition metal compounds is the comparison with the reactivity pattern of isolobal alkynes of the type $RC\equiv CR'$ (R, R′ = alkyl, aryl). The complex chemistry of alkynes is, amongst other factors, characterized by cyclooligomerization processes in the coordination sphere of the transition metal center. Corresponding oligomers of isoelectronic phosphaalkynes have been synthesized recently, and products of di-, tri-, and tetramerization on transition metal centers were successfully isolated. Dimerization to 1,3-diphosphete ligands is the preferred reaction in such cases. The head-to-tail dimerization on 14-valence electron (VE) complexes of cobalt,[7] rhodium,[8] and iron[9] and on 12VE fragments of zirconium and hafnium[10] occurred with the formation of compounds of type **A** (cot = cyclooctatetraene). In comparison, dimerization to 1,2-diphosphete (complex **B**) is rare, but has been observed in the coordination sphere of titanium complex fragments.[11]



A

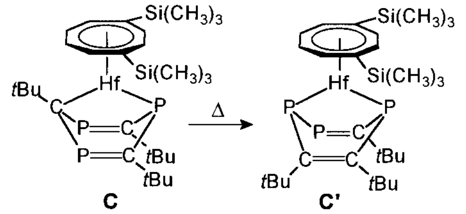


B

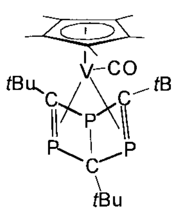
M = Co, Rh; L = η^5-C_5R_5; R = H, Me

M = Zr, Hf; L = cot

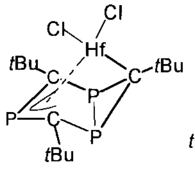
M = Fe; L = 3 CO



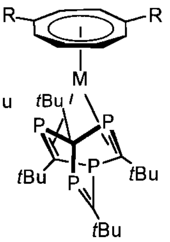
C **C′**



D



E



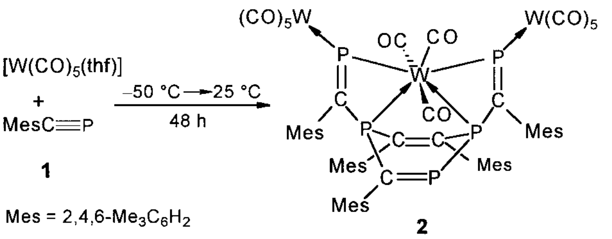
F

M = Hf; R = $SiMe_3$
M = Zr; R = H

The number of known trimerization products is much smaller than the number of dimers. The synthesis of trimeric phosphaalkyne derivatives succeeded with (η^4-butadiene)[η^8-1,4-bis(trimethylsilyl)cyclooctatetraene]hafnium as the starting material.[12] By reaction with $tBuC\equiv P$, compound **C** was obtained initially. Thermolysis of **C** led to an intramolecular rearrangement to form **C′**, whose composition was determined on the basis of $^{31}P\{^1H\}$ NMR spectroscopic data. Furthermore, vanadium complex **D** with a 1,3,5-triphospha-Dewar-benzene ligand[13] as well as the hafnium complex **E** with the 1,3,5-triphosphabicyclo[3.1.0]hexene ligands[14] have also been described. The only known phosphaalkyne tetramerization product is the tetraphosphabarrelene complex **F**.[15]

Here we report the synthesis and characterization of the first pentamerization product from mesityl-phosphaalkyne and $[W(CO)_5(thf)]$.[16] These studies are part of our investigations into the formation of complexes with a metal–phosphorus triple bond by three-component reactions between $[(RO)_6W_2]$ (R = tBu, 2,5-$Me_2C_6H_4$) and the phosphaalkyne in the presence of $[M(CO)_5thf]$ (M = Cr, W).[17]

The reaction of $MesC\equiv P$ (**1**) with $[W(CO)_5(thf)]$ at −50 °C in THF/*n*-hexane yielded a product mixture from which the pentamerization product **2** was isolated in 10% yield after column chromatographic workup [Eq. (1)]. The separation and characterization of the other products proved to be very complex, although spectroscopic data indicated the presence of compounds with 1,3-diphosphete ligands. Compound **2** is an orange-red crystalline solid which is stable for a short time in air and which dissolves well in toluene and THF. Solutions of **2** are unstable with respect to thermolysis and photolysis. The molecular structure of **2**[18] (Figure 1) shows a basic framework of a metalla-norbornadiene formed by the atoms P(3), C(15), P(5), P(4), C(17), C(16), and W(1) and extended by two phosphaalkyne units in the 1,4-position. The basic framework is similar to the trimerization product of $tBuC\equiv P$ in **C′** and has been structurally verified. The central feature of compound **2** is the tungsten atom W(1),[19] which is sevenfold coordinated by three CO groups and the phosphorus atoms P(1) to P(4) of the pentamer. The W(1)–P(1) and W(1)–P(2) bond lengths of 2.5398(14) and 2.514(2) Å are within the range of typical W–P bonds, such as in $[Ph_3P\{W(CO)_5\}]$ (2.544 Å).[20] The bond lengths W(1)–P(3) and W(1)–P(4) with 2.494(2) and 2.459(2) Å are slightly shortened in comparison. The phosphorus atoms P(1) and P(2) are also bonded to $[W(CO)_5]$ units and to C(18) or C(14). These bond distances (1.707(5) and 1.710(5) Å) lie within the range of slightly elongated P=C bonds.[21] The metalla-norbornadiene fragment is bonded through P(3) and P(4) to the carbon atoms of the phosphaalkyne units, C(14)/P(2) and C(18)/P(1). The bond lengths are 1.801(5) and 1.775(5) Å and are therefore in the range of slightly elongated P–C single bonds (1.84 Å[22]). Within the boat-shaped six-membered ring, there is a P–P bond between the atoms P(4) and P(5). The bond length of



(1)

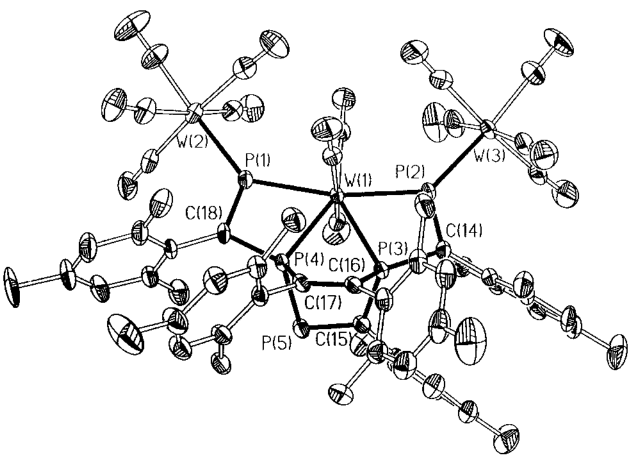
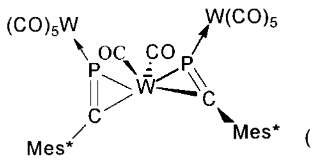


Figure 1. Structure of **2** in the crystal (ORTEP, vibrational ellipsoid with 50 % probability, hydrogen atoms omitted). Selected bond lengths [Å] and angles [°]: P(1)–C(18) 1.707(5), P(2)–C(14) 1.710(5), P(1)–W(1) 2.5398(14), P(2)–W(1) 2.514(2), P(1)–W(2) 2.453(2), P(2)–W(3) 2.460(2), P(4)–C(18) 1.775(5), P(4)–C(17) 1.849(6), P(4)–P(5) 2.249(2), P(4)–W(1) 2.459(2), P(5)–C(15) 1.695(5), P(3)–C(14) 1.801(5), P(3)–C(15) 1.872(5), P(3)–C(16) 1.916(5), P(3)–W(1) 2.494(2), C(16)–C(17) 1.359(7); P(3)-C(16)-C(17) 109.0(4), C(17)-C(16)-C(37) 124.4(4), C(37)-C(16)-P(3) 126.6(4), P(3)-C(15)-P(5) 114.6(3), P(3)-C(15)-C(28) 122.1(4), C(28)-C(15)-P(5) 123.1(3), C(14)-P(2)-W(1) 100.4(2), C(18)-P(1)-W(1) 98.9(2).

2.249(2) Å is in the range of a P–P single bond (β-P_4: 2.204 Å[23]). The distance between P(5) and C(15) is 1.695(5) Å and corresponds to the P–C bond length in phosphaalkenes.[22] There is also a typical C–C double bond of 1.359(7) Å between the atoms C(16) and C(17). The sp^2 hybridization of the atoms C(15) and C(16) is also confirmed by consideration of the relevant bond angles. The distances between P(3) and C(15) (1.872(5) Å) and between P(3) and C(16) (1.916(5) Å) correspond to P–C single bonds, which is also the case for the bond distance of 1.849(6) Å for P(4)–C(17).

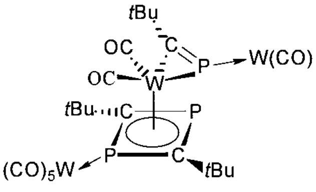
In the ^{31}P NMR spectrum of **2**, five groups of signals for the different phosphorus atoms were observed. Two doublets at $\delta = 497.6$ and 456.1 are assigned to P(2) and P(1) with J(P,P) coupling constants of 45 and 42 Hz, respectively. Each doublet has a satellite pair with a coupling constant ^1J(W,P) of 190 Hz, which is within the usual range of coupling constants between a phosphorus atom and a tungsten atom of a $[W(CO)_5]$ group. The P–P couplings of these signals are found within the signal groups of P(3) and P(4) at $\delta = 50.8$ and 10.4. These nuclei couple both with each other and with the atom P(5), which displays a large ^1J(P,P) coupling constant of 280 Hz as a result of the proximity to P(4). A somewhat larger coupling constant (354 Hz) was obtained for the coupling between the neighboring P atoms in the hafna-norbornadiene complex **C′**.[12] The coupling constant for coupling between P(4) and the W atom of the central $[W(CO)_3]$ group was determined to be 108 Hz, but it was not possible to resolve the equivalent coupling for P(3).

It was not possible to derive any rules for the degree of oligomerization of phosphaalkynes from an examination of the existing complex fragments in **A**–**F** and **2**. For example, dimerization occurs most commonly in the coordination sphere of 14VE fragments. Although dimerization takes place to a certain extent with 12VE complex fragments, mainly trimerization, tetramerization, and now also pentamerization are observed. Much more significant than the number of valence electrons of the complex fragment are the steric and electronic properties of the phosphaalkyne reactant. The use of Mes*C≡P in reaction (1) resulted in the formation of complex **3**, in which the phosphaalkynes are only coordinated "side-on".[24] In contrast, with tBuC≡P the cyclodimerization product **4** was obtained exclusively.[17a] The results presented here show that a pentamerization product is also accessible with MesC≡P. The formation of **2** can be explained by various dimerization, Diels–Alder, and ring-opening reactions. In addition, the ability of $[W(CO)_5]$ groups to eliminate CO to form $[W(CO)_6]$[25] ultimately enables the formation of the central $[W(CO)_3]$ complex unit. It can be predicted that the variation of the steric and also the electronic properties of the substituents on the phosphaalkyne (e.g. in R_2NC≡P[26] and –OC≡P[27]) will have a significant influence on the reactivity and thus offer access to further novel products.



Mes* = 2,4,6-$tBu_3C_6H_2$

3



4

Experimental Section

A solution of **1** (162 mg, 1 mmol) in n-hexane (20 mL) was cooled to −50 °C. At this temperature, a 0.04 M solution of $[W(CO)_5(thf)]$ (1 mmol) in THF (25 mL) was added, and the reaction solution was reduced to about 20 mL. Then the solution was warmed over a period of 15 h to room temperature and then stirred for a further 48 h. Subsequently all volatile components were removed under vacuum (10^{-3} Torr). Three such batches were combined and purified by column chromatography. After separation of a bright red fraction (n-hexane), an orange fraction was eluted with n-hexane/toluene (1/1), from which 100 mg (10 %) of **2** were isolated. ^{31}P{^{1}H} NMR (101.256 MHz, [D$_6$]benzene, 298 K, 85 % H_3PO_4 ext.): $\delta = 497.6$ (P_A: d; $^2J(P_A,P_C) = 45$, $J(W,P_A) = 190$ Hz), 456.1 (P_B: d; $^2J(P_B,P_D) = 42$, $J(W,P_B) = 190$ Hz), 370.7 (P_E: dd; $^1J(P_E,P_D) = 280$, $^2J(P_E,P_C) = 35$ Hz), 50.8 (P_C: ddd; $^2J(P_C,P_A) = 45$, $^2J(P_C,P_E) = 35$, $^2J(P_C,P_D) = 15$ Hz), 10.4 (P_D: ddd; $J(P_D,P_E) = 280$, $^2J(P_D,P_B) = 42$, $^2J(P_D,P_C) = 14$, $J(W,P_D) = 108$ Hz); ^{1}H NMR (250.133 MHz, [D$_6$]benzene, 298 K, TMS): $\delta = 1.400$, 1.422, 1.720, 1.819, 1.838, 1.900, 1.937, 1.979, 2.002, 2.061, 2.113, 2.163, 2.780, 2.864, 3.229 (CH_3, each s, 3H), 6.82–5.71 (arom. CH, 10s, 1H each); FT-IR (Nujol): $\tilde{\nu}$(CO) = 2075(s), 2065(s), 2041(m), 1987(w), 1962(sh), 1950(vs), 1938(vs), 1931(vs), 1925(vs) cm^{-1}; elemental analysis calcd for $C_{63}H_{55}O_{13}P_5W_3$ (1726.54): C 43.10, H 3.10; found: C 43.50, H 3.35.

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[18] X-ray crystal structure data for **2**$\cdot C_7H_8$: Stoe IPDS diffractometer, $Mo_{K\alpha}$ ($\lambda = 0.71069$ Å), structure solution with direct methods, least-squares method, all non-hydrogen atoms were anisotropically refined. The hydrogen atoms were fixed in idealized positions and refined isotropically as riding models. $C_{63}H_{55}O_{13}P_5W_3 \cdot C_7H_8$, $M_r = 1818.60$, crystal dimensions $0.45 \times 0.19 \times 0.08$ mm^3, triclinic, space group $P\bar{1}$ (no. 2); $a = 15.985(3)$, $b = 16.797(3)$, $c = 17.358(4)$ Å, $\alpha = 90.99(3)$, $\beta = 111.35(3)$, $\gamma = 116.62(3)^\circ$, $T = 200(1)$ K, $Z = 2$, $V = 3788.5(13)$ Å^3, $\rho_{calcd} = 1.594$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 47.05$ cm^{-1}; of 13638 independent reflections ($2\theta_{max} = 53^\circ$), 12004 were observed with $F_o = 4\sigma(F_o)$; 900 parameters, $R_1 = 0.0361$, $wR_2 = 0.1069$; structure solution and refinement with the programs SHELXS-86[28a] and SHELXL-93.[28b] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-125116. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Facile, Novel Methodology for the Synthesis of Spiro[pyrrolidin-3,3′-oxindoles]: Catalyzed Ring Expansion Reactions of Cyclopropanes by Aldimines**

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The spiro[pyrrolidin-3,3′-indole] ring system is a recurring structural motif in a number of natural products such as vinblastine and vincristine that function as cytostatics and are of prime importance in cancer chemotherapy.[1] The related spiro[pyrrolidin-3,3′-oxindole] ring system has been identified in a number of other cytostatic alkaloids, exemplified by spirotryprostatin A and strychnophylline.[2] Moreover, these structures embody stereochemical and structural complexities that continue to challenge the synthetic chemist.[3, 4] In combination, these factors have driven the development of novel, versatile, and efficient methods aimed at the synthesis of the spiro[pyrrolidin-3,3′-oxindole] moiety and related structures, as exemplified recently in the elegant total synthesis of spirotryprostatin by Danishefsky et al. and of aspidophytine by Corey et al.[5] We have been interested in the development of a variety of methods for the stereocontrolled synthesis of alkaloids.[6] Herein we report a novel

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