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[15] The absolute configuration of the tetrahydronaphthalenoxazole derivative (+)-**5** was concluded from comparison of its optical rotation ($[\alpha]_D^{20} = +7.4$; $c = 1$ in $CHCl_3$) with the analogous benzoxazole derivative[13] {$[\alpha]_D^{20} = +7.4$; $c = 2$ in $CHCl_3$) and by the absolute configuration of the irradiation product **2**.

[16] The reactions were conducted at the indicated temperature with toluene as the solvent (0.15 M solution of **1**). Further details regarding the irradiation procedure can be found in: T. Bach, J. Schröder, *J. Org. Chem.* **1999**, *64*, 1265–1273. The *ee* values (*ee* = [(−)-**2** − (+)-**2**)]/[(−)-**2**+(+)-**2**]) were determined by HPLC analysis (column: Chiracel OD; eluent: hexane/2-propanol, 92/8) of the crude product mixture. The separation of host and product is possible by flash chromatography (pentane/*tert*-butylmethylether, 1/2). Both enantiomers of the host **5** were employed. Naturally, the direction of the face discrimination changes if (+)-**5** is replaced by (−)-**5**.

[17] Crystal data of host (−)-**4** ($C_{22}H_{37}NO_3 \cdot CH_2Cl_2$, $M_r = 448.45$): crystal size $0.3 \times 0.3 \times 0.15\ mm^3$, orthorhombic, space group $P2_12_12_1$, $a = 852.0(1)$, $b = 1212.3(1)$, $c = 2410.5(1)$ pm, $V = 2489.9(4)$ Å^3, $\rho_{calcd} = 1.196\ g\,cm^{-3}$, $Z = 4$, $F(000) = 968$, $\mu = 2.516\ mm^{-1}$, Enraf-Nonius-CAD4 diffractometer, $\lambda = 1.54178$ Å, ω-scans, 4875 measured reflections ($-h$, $+k$, $\pm l$), $\Theta_{max} = 65°$, 4245 independent and 3575 observed reflections [$F \geq 4\sigma(F)$], 272 refined parameters, $R = 0.0608$, $wR^2 = 0.2080$, max. residual electron density 0.22 e Å^{-3}, direct methods, carbon-bound hydrogen atoms calculated, N–H atom refined. 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-142268. 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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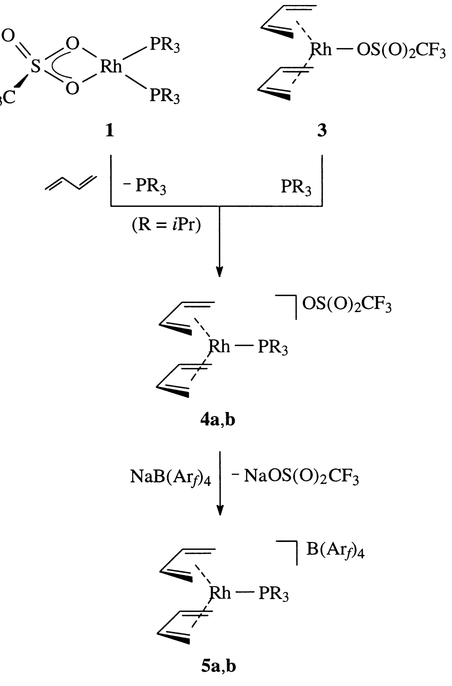
The Rhodium-Catalyzed Cyclotetramerization of Butadiene: Isolation and Structural Characterization of an Intermediate**

Marco Bosch, Maurice S. Brookhart, Kerstin Ilg, and Helmut Werner*

We have recently shown that the square-planar sulfonatorhodium(I) complex *cis*-[Rh{η^2-$O_2S(O)CF_3$}($PiPr_3)_2$][1] (**1**) is an active catalyst for the polymerization of butadiene.[2] A remarkable side product of this process was found to be 1,5,9,13-cyclohexadecatetraene. Although in the initial studies the overall yield of this cyclotetramer was rather low (< 5 %), we became interested to find out whether there could be a relationship between this reaction and the well known, "naked-nickel"-catalyzed, cyclo*tri*merization of butadiene discovered by Wilke et al.[3, 4] Since a key step in the reaction leading to *all-trans*-1,5,9-cyclododecatriene is the oxidative coupling of two butadiene ligands in the coordination sphere of nickel(0) to give the labile octadienediylnickel(II) derivative [Ni(η^3:η^3-C_8H_{12})],[4] we focused our efforts on detecting or, if possible, even isolating a related rhodium complex containing a C_8H_{12} ligand.

In a first attempt to elucidate the mechanism of the rhodium-catalyzed cyclo*tetra*merization of butadiene, we treated the triflate [Rh{μ-$O_2S(O)CF_3$}($C_8H_{14})_2]_2$ (**2**) with C_4H_6 and isolated the neutral bis(butadiene)rhodium(I) complex [Rh{η^1-$OS(O)_2CF_3$}(*s-cis*-η^4-$C_4H_6)_2$] (**3**) in almost quantitative yield.[5] Since it was known that the addition of one equivalent of tricyclohexylphosphane to the nickel(0) compound [Ni(*s-cis*-η^4-$C_6H_{10})_2$] induces the coupling of the two coordinated 2,3-dimethylbutadiene ligands to generate the substituted octadienediylnickel(II) complex [Ni(η^1:η^3-$C_{12}H_{20}$)(PCy_3)],[6] we also treated compound **3** with PCy_3. However, under the conditions used (acetone, 5 min, 25 °C), instead of a C–C coupling a substitution of the coordinated triflate occurred and the ionic product [Rh(*s-cis*-η^4-$C_4H_6)_2(PCy_3)$]OTf (**4b**) was formed (Scheme 1, $OS(O)_2CF_3$ = OTF). The triisopropylphosphane analogue **4a**, which like **4b** is a white, moderately air-stable solid, is accessible in a similar way.[5] Salt metathesis of **4a** and **4b** with $NaB(Ar_f)_4$ (Ar_f = 3,5-bis(trifluoromethyl)phenyl) affords the corresponding compounds **5a** and **5b** in 83 and 86 % yield, respectively.

Although both **4a** and **4b** are stable in solution at room temperature and thus can be characterized by ^1H, $^{13}C\{^1H\}$,



Scheme 1. **a**: R = *i*Pr; **b**: R = Cy.

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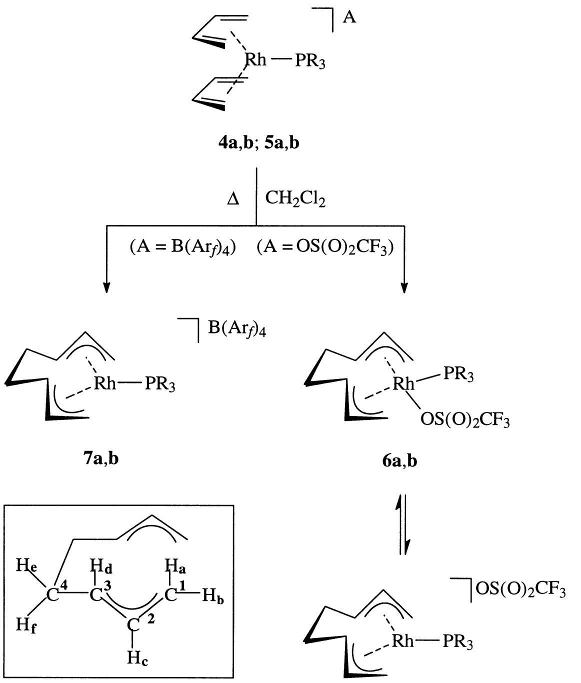
and $^{31}P\{^1H\}$ NMR spectroscopy, they react in CH_2Cl_2 under reflux (12 h for **4a** and 6 h for **4b**) to give, after recrystallization from CH_2Cl_2/pentane, the isomeric octadienediyl complexes **6a** and **6b** (Scheme 2). The red crystalline solids are soluble in polar organic solvents and can be stored without decomposition under argon at room temperature for days.



Scheme 2. **a**: R = *i*Pr, **b**: R = Cy.

The result of the X-ray crystal structure analysis of **6a** is shown in Figure 1.[7] The coordination geometry around the rhodium(III) center is distorted octahedral with atoms P1, C1, C6, and C8 occupying the equatorial and C3 and O1 the axial positions. The bond lengths Rh1–C1, Rh1–C3, C1–C2, and C2–C3 together with the bond angle C1-C2-C3 are in good agreement with those in related η^3-allylrhodium[5, 8] and octadienediylruthenium complexes.[9] In contrast to the C1-C2-C3 unit, the C6-C7-C8 fragment is slightly distorted which results in a lengthening of the two C–C bonds by approximately 0.05 Å and of the Rh–C bonds by approximately 0.1 Å. An even more characteristic feature is that the Rh1–O1 bond length (2.473(3) Å) is significantly longer than in the precursor molecule **3** (2.289(1) Å),[5] which explains why, as indicated by the IR spectrum of **6a** in CH_2Cl_2, a dissociation of the neutral compound into the triflate anion and the cation $[Rh(\eta^3{:}\eta^3\text{-}C_8H_{12})(PiPr_3)]^+$ occurs (see Scheme 2). To the best of our knowledge, compounds **6a** and **6b** are the first octadienediyl complexes of the Group 9 elements (Co, Rh, Ir) described in the literature.[10]

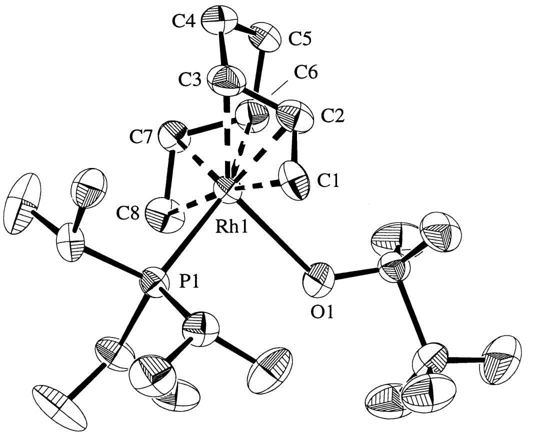


Figure 1. Molecular structure of **6a** in the crystal. Selected bond lengths [Å] and angles [°]: C1-C2 1.398(10), C2-C3 1.412(10), C3-C4 1.501(12), C4-C5 1.528(12), C5-C6 1.508(10), C6-C7 1.461(17), C7-C8 1.453(17), Rh1-C1 2.158(17), Rh1-C3 2.179(6), Rh1-C6 2.262(5), Rh1-C8 2.286(14), Rh1-P1 2.478(1), Rh1-O1 2.473(3); C1-C2-C3 116(1), C6-C7-C8 112(2).

Similarly to **4a** and **4b**, also the $B(Ar_f)_4$ complexes **5a** and **5b**, upon heating in dichloromethane, undergo a C–C coupling process to give the corresponding ionic octadienediylrhodium(III) derivatives **7a**, **b** in approximately 70% yield (Scheme 2). From a high-level density functional theory (DFT) study using $[Rh(s\text{-}cis\text{-}\eta^4\text{-}C_4H_6)_2(PH_3)]^+$ and $[Rh(\eta^3{:}\eta^3\text{-}C_8H_{12})(PH_3)]^+$ as model compounds, a difference in energy of $\Delta G = -4.1$ kcal mol^{-1} between the two isomers was calculated.[11] This indicates that the C–C coupling reaction is thermodynamically favored. The conversion of the bis(diene) compounds **4a**, **b** and **5a**, **b** to their octadienediyl derivatives **6a**, **b** and **7a**, **b**, respectively, follows a first-order rate law. In nitromethane, the reactions of **4b** and **5b** are somewhat faster than those of the $PiPr_3$ analogues **4a** and **5a**. The free energy of activation $\Delta G^{\neq}$ has been determined as 23.7(1) kcal mol^{-1} (for **4a** and **5a**) and 23.3(1) kcal mol^{-1} (for **4b** and **5b**).

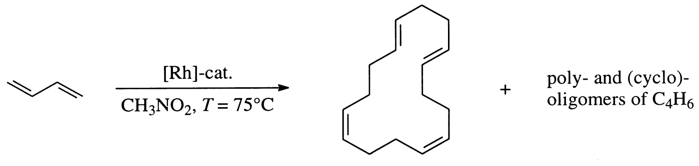
The observation that **1** reacts under mild conditions with C_4H_6 to give **4a** in nearly quantitative yield (Scheme 1) supports the assumption that the bis(diene) complex **4a** plays an important role as an intermediate in the poly- and oligomerization of butadiene catalyzed by triflate **1**. In order to prove this, we treated **4a** as well as **4b** at elevated temperatures with an excess of C_4H_6 and found that a mixture of (cyclo)oligomers and polymers of butadiene in a ratio of 43:57 (**4a**) and 34:66 (**4b**) is formed (see Table 1, entry 1 and 2). GC/MS analysis of the mixture of products revealed that the oligomeric fraction predominantely (ca. 90%) consists of a mixture of C_{12} and C_{16} hydrocarbons. Among the tetrameric fraction, a high selectivity, 83% with **4a** and 79% with **4b** as catalyst, for the *cis,cis,trans,trans* isomer of 1,5,9,13-cyclohexadecatetraene (**8**) is observed (Scheme 3). This results in an overall selectivity for **8** in the oligomeric fraction of 34 and 41%, respectively. When the catalyst is prepared in situ from **2** and two equivalents of $PiPr_3$ (Table 1, entry 3), both the activity and selectivity compare well with that for **4a**. Raising the temperature to 95 °C (Table 1, entry 4) leads to a higher selectivity for the tetrameric products in the oligomeric fraction (60%) but also to a significant increase of the relative amount of polymeric material.

The ^{13}C NMR spectrum of **8**, which can be isolated as a colorless oil, shows four signals of equal intensity at around $\delta = 129$ for the CH carbon atoms, from which the configuration was derived as *c,c,t,t* (and not *c,t,c,t*).

Table 1. Metal-catalyzed poly- and oligomerization reactions of butadiene. Standard conditions for entries 1–4: CH_3NO_2 (10 mL), C_4H_6 (3 mL), 5 h, 75 °C.

Entry	Catalyst	Cat.-loading[a] [mol %]	Yield [%]	TON[b]	Polymer: Oligomer[c]	Product distribution of oligomeric fraction [%]				
						C_8	C_{12}	C_{16}[d]	C_{20}	C_{24}
1	**4a**	0.33	23	69	57:43	–	49	41 (34)	6	4
2	**4b**	0.30	27	88	66:34	–	37	52 (41)	7	4
3	**2** + 2 P*i*Pr$_3$	0.56	39	70	55:45	–	46	44 (31)	6	4
4[e]	**2** + 2 P*i*Pr$_3$	0.45	47	104	72:28	–	28	60 (39)	6	6
5	$[Ni(C_3H_5)_2]$/ $[NiCl(C_3H_5)]_2$[f]	0.26	58	224	56:44	9	41	8 (–)	22	20

[a] Based on the amount of butadiene employed. [b] TON = turnover number = {amount of C_4H_6 [mmol]}/[amount of catalyst [mmol]}. [c] The polymeric product consists of oligobutadienes $(C_4H_6)_n$ with $n \geq 8$. [d] Percentage of *cis,cis,trans,trans*-1,5,9,13-cyclohexadecatetraene (**8**) in parenthesis. [e] C_4H_6 (5 mL), 95 °C. [f] In toluene, 85 h, room temperature.



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Scheme 3. [Rh]-cat. = **4a**, **4b** or **2** + 2 P*i*Pr$_3$.

In summary, it is rather surprising that, despite the numerous studies about the poly- and oligomerization reactions of butadiene, the transition metal catalyzed cyclo*tetra*merization of C_4H_6 has received little attention in the literature.[4a] There are two reports by Dzhemilev et al.[12] and Miyake et al.[13] who generated a catalytic system in situ, either from $TiCl_4/Et_2AlCl$ and 2-vinylfuran or from π-allylnickel(II) compounds. With the titanium system, a mixture of cyclic *all-trans* tri- and tetramers in a ratio of 7:3 was formed, whereas with the nickel(II) compound a variety of poly- and (cyclo)oligomers of butadiene was obtained (Table 1, entry 5). In contrast, the phosphanerhodium(I) complexes **4a**, **4b**, and **2**, if used as catalysts, have the advantage of a narrow product distribution and a high selectivity for **8** in the oligomeric fraction. With regard to the role that the isolated octadienediyl complex **6a** plays in the rhodium-catalyzed cyclooligomerization of C_4H_6, the results of preliminary NMR experiments indicate that in the initial stage of the reaction the formation of **6a** is the rate-determining step and the bis(diene) compound **4a** is the catalyst resting state.

Experimental Section

6a: A solution of of **4a** (175 mg, 0.34 mmol) in dichloromethane (20 mL) was heated under reflux for 12 h. A gradual change of color from light red to dark red occurred. After the reaction mixture was cooled to room temperature, the solvent was removed in vacuo. The oily residue was washed with pentane (3 × 5 mL) and the resulting red solid recrystallized from dichloromethane/pentane (1:5); yield 131 mg (74%); m.p. 104 °C (decomp); IR (CH_2Cl_2): $\tilde{\nu} = 1270-1260$ ($OSO_{asymm.}$), 1239 ($CF_{symm.}$), 1162 ($CF_{asymm.}$), 1031 cm^{-1} ($OSO_{symm.}$); ^1H NMR (400 MHz, CD_2Cl_2):[14] $\delta = 5.23$ (ddd, 2H, $^3J(H,H) = 11.6$ Hz, $^3J(H,H) = 10.6$ Hz, $^3J(H,H) = 7.0$ Hz; H_c), 4.88 (dd, 2H, $^3J(H,H) = 7.0$ Hz, $^4J(H,H) = 1.8$ Hz; H_a), 4.21 (br ddd, 2H, $^3J(H,H) = 10.6$ Hz, $^3J(H,H) = 3.5$ Hz, $^4J(H,H) = 1.8$ Hz; H_d), 3.07 (dd, 2H, $^3J(H,H) = 11.6$ Hz, $^3J(P,H) = 6.3$ Hz; H_b), 2.63 (m, 3H; PC*H*CH$_3$), 2.28 (m, 2H; H_e), 1.53 (m, 2H; H_f), 1.28 (dd, 9H, $^3J(P,H) = 14.3$ Hz, $^3J(H,H) = 7.0$ Hz; PCHC*H*$_3$), 1.15 (dd, 9H, $^3J(P,H) = 13.8$ Hz, $^3J(H,H) = 7.3$ Hz; PCHC*H*$_3$); $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2): $\delta = 97.0$ (d, $^1J(Rh,C) = 5.3$ Hz; C^2), 91.1 (dd, $^1J(Rh,C) = 8.4$ Hz, $^2J(P,C) = 6.4$ Hz; C^3), 69.9 (dd, $^1J(Rh,C) = 6.1$ Hz, $^2J(P,C) = 3.8$ Hz; C^1), 29.2 (s; C^4), 27.1 (d, $^1J(P,C) = 18.3$ Hz; P*C*HCH$_3$), 19.8, 19.7 (both s; PCH*C*H$_3$); $^{19}F\{^1H\}$ NMR (376.4 MHz, CD_2Cl_2): $\delta = -78.8$ (s); $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2): $\delta = 40.2$ (d, $^1J(Rh,P) = 170.4$ Hz). For assignment of protons and carbon atoms of the C_8H_{12} ligand see Scheme 2.

8: The cyclotetramer was obtained after fractional distillation of the combined oligomeric fractions obtained with **4a**, **4b** and **2**/P*i*Pr$_3$ as catalysts (Table 1, entries 1–4) in a Kugelrohr apparatus; colorless oil; b.p. 100–110 °C (1 mbar); MS (70 eV): m/z: 216 [M^+]; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 5.41$ (br s, 8H, CH), 2.08 (br s, 16H, CH_2); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): $\delta = 129.9$, 129.7, 129.6, 129.4 (all s, CH), 32.6, 28.0, 27.7 (all s, CH_2).

The catalytic reactions were carried out as follows: In a typical experiment, a 50-mL glass autoclave was loaded with a solution of **4a** (58 mg, 0.11 mmol), **4b** (65 mg, 0.10 mmol), or a mixture of **2** (89 mg, 0.09 mmol) and P*i*Pr$_3$ (37 mL, 0.18 mmol), in freshly distilled nitromethane (10 mL) and butadiene (3 mL, 33.8 mmol). The mixture was heated for 5 h at 75 °C and then cooled to room temperature. The solvent and excess butadiene were removed, the oily residue was extracted with pentane (2 × 35 mL), and the extract was flash-chromatographed on Al_2O_3 (neutral, activity grade V). Evaporation of the solvent afforded in each case a waxy colorless product which was analyzed by GC/MS; yield 413 mg (**4a**), 488 mg (**4b**), 708 mg (**2**, entry 3) and 1488 mg (**2**, entry 4, Table 1). The relative amount of polymer in the isolated product was calculated from the difference between the yield of product and the yield of oligomers determined by the sum of the integrated signals in the GC spectrum for the C_8–C_{24} hydrocarbons.

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[7] Data for the X-ray structure analysis of **6a**: Crystals from dichloromethane/pentane, $C_{18}H_{33}F_3O_3PRhS$ ($M_r = 520.46$); crystal size $0.19 \times 0.18 \times 0.16$ mm; monoclinic, space group $P2_1/c$, $Z = 4$, $a = 8.498(1)$, $b = 15.383(1)$, $c = 16.899(2)$ Å, $\beta = 94.18(2)^\circ$, $V = 2201.9(5)$ Å^3, $\rho_{calcd} = 1.570$ g cm^{-3}; $T = 173(2)$ K; $2\theta = 50.04^\circ$; 17827 reflections measured, 3884 were unique, ($R_{int} = 0.0569$), and 2922 observed ($I > 2\sigma(I)$); IPDS (Stoe), $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), graphite-monochromated; Lp correction. The structure was solved by direct methods and refined with the full-matrix, least-square method; $R_1 = 0.0360$, $wR_2 = 0.0877$ (for 2922 reflections with $I > 2\sigma(I)$), $R_1 = 0.0509$, $wR_2 = 0.0936$ (for all 3884 data); data-to-parameter ratio 11.99; residual electron density $+0.797/-0.636$. All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the refinement of the hydrogen atom positions. The octadienediyl ligand in **6a** is disordered and found with an occupancy of 0.69:0.31, it was refined anisotropically with restrains.Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-139992. 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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Novel 1,2,4-Triphosphole and 1,2,3-Triphosphetene Derivatives from *N,N'*-Bis(2,2-dimethylpropyl)benzimidazolin-2-ylidene and Phosphaalkynes[**]

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Halocarbenes react with phosphaalkynes primarily to form unstable 2*H*-phosphirenes, which undergo rearrangements through [1,3] halogen shift to yield the isomeric 1*H*-phosphirenes.[1] Addition of the phosphanylsilylcarbene (Bertrand carbene) to *tert*-butylphosphaacetylene affords the stable $1\lambda^5,2\lambda^3$-diphosphetene (probably due to the ring expansion of 2-phosphino-2*H*-phosphirene, which is an intermediate produced through a [1+2] cycloaddition).[2] The analogous reactions of silylenes, germylenes, and stannylenes with $P{\equiv}CR$ produce three- or four-membered-ring systems containing a phosphaalkene structural element.[3] However, to date nothing has been reported about the reactivity of the intensively studied N-heterocyclic carbenes[4] toward phosphaalkynes.

We now report the unexpected formation of functionalized 1,2,4-triphosphole[5] and 1,2,3-triphosphetene[6] derivatives by reaction of the recently discovered stable N-heterocyclic annelated carbene *N,N'*-bis(2,2-dimethylpropyl)benzimidazolin-2-ylidene (**1**),[7] with the phosphaalkyne $P{\equiv}CtBu$ (**2a**) or $P{\equiv}C\text{-}NiPr_2$ (**2b**).

Treatment of carbene **1** with the phosphaacetylene **2a** at room temperature in a molar ratio of 1:1 affords the crystalline adduct **5** after 48 h in a near quantitative yield (calculated from **2a**) (Scheme 1). The $^{31}P\{^1H\}$ NMR spectrum shows an AMX spin system. The positions of the signals and corresponding couplings of the resonances, and in particular the characteristic size of the $^1J(P1,P2)$ coupling of 528.1 Hz, are similar to those reported for the 1,2,4-triphosphole $P_3C_2tBu_2R$ ($R = CH(SiMe_3)_2$)[5a]. The ^1H and ^{13}C NMR parameters also fit well with the literature data.[5a] Information on the structure and bonding in the new 1,2,4-triphosphole derivative **5** is provided by the X-ray crystal structure analysis (Figure 1). The phosphorus heterocycle is almost planar (maximum deviation from the best plane through the ring is 0.016 Å for P2. The sum of the angles at the tricoordinate phosphorus atom is 359.8°). The $\sigma^3\text{-P-C}_{Ring}$ bond (1.721(2) Å) is noticeably shorter than the other $\sigma^2\text{-P-C}_{Ring}$ bonds (1.734(2)–1.738(2) Å). These structural parameters indicate a completely delocalized 1,2,4-triphosphacyclopentadiene system, which is in agreement with the results recently published by Niecke and Nixon et al.[5b] on aromatic 1-[bis(trimethylsilyl)methyl]-3,5-bis(trimethylsilyl)-1,2,4-triphos-

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