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Synthesis and molecular structure of mesocyclic 3,7-dimethyl-1,1,5,5-tetraphenyl-1.lambda.5,5.lambda.5-diphosphocin, a 1,5-bis(.lambda.5-phospha)cyclooctatetraene

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Synthesis and Molecular Structure of Mesocyclic 3,7-Dimethyl-1,1,5,5-tetraphenyl-1λ^5,5λ^5-diphosphocin, a 1,5-Bis(λ^5-phospha)cyclooctatetraene

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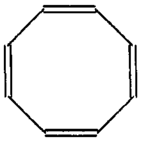
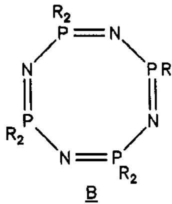
Summary: Cyclization of 1,1-bis[(diphenylphosphino)methyl]ethene (1) with 3-chloro-2-(chloromethyl)-1-propene results in the formation of the 3,7-dimethylene-1,1,5,5-tetraphenyl-1,5-diphosphocanium dichloride (2). The cyclic bis(ylide) was obtained upon double deprotonation with strong base and undergoes a double exo–endo proton-transfer rearrangement to give the title compound 3,7-dimethyl-1,1,5,5-tetraphenyl-1λ^5,5λ^5-diphosphocin (3). Both 2 and 3 have been characterized on the basis of ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra, mass spectrometry, and elemental analysis. Orange-yellow crystals of composition 3·0.5Et$_2$O grown from diethyl ether at −25 °C have been studied by X-ray crystallography: space group $C2/c$, a = 25.003 (4) Å, b = 16.773 (1) Å, c = 15.614 (2) Å, β = 116.781 (6)°, V = 5845.74 Å^3, Z = 8. The mesocycle shows a puckered tublike conformation with two conjugatively isolated methallylic fragments connected via the two λ^5-phosphorus atoms, which act as barriers against full π-electron delocalization, owing to the nodal planes of their d functions.

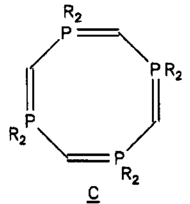
The special features of cyclooctatetraene (COT) with its nonaromatic system of eight π-electrons (A) have attracted considerable and unrelenting interest for almost a century.[1]



A



B



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COT's with heteroatoms, however, are less well represented in the literature, and λ^5-*phospha*-COT molecules in particular are not well documented.[2] This is surprising, since the rich chemistry of cyclotetraphosphazenes with their (R$_2$PN)$_4$ skeleton (B)[3] suggests great potential for a related, isoelectronic, (R$_2$PCH)$_4$ (C) series. This resembles the situation with benzene and the *phospha*benzenes (phosphorins), where only the chemistry of mono-λ^5-phosphorins has been developed.[4] Di-λ^5-phosphorins are still rare,[5] and only few tri-λ^5-phosphabenzenes are documented.[6]

We now report the synthesis of the first 1,5-bis(λ^5-phospha)cyclooctatetraene and describe its crystal and molecular structure. The preparative procedure is based on a method successfully applied very recently for the synthesis of 1λ^5,3λ^5-diphosphorins.[5a] The title compound is of great general importance for phosphorus heterocyclic chemistry but also can function as a powerful ligand for transition metals owing to its two allylic donor systems. For the related 1λ^5,3λ^5-diphosphorins the excellent ligand properties of the methallylic unit have already been demonstrated.[7]

Eight-membered heterocycles containing two phosphorus atoms in the 1,5-positions have been described previously,[8,9] but efforts to obtain the COT-analogous bonding situation in these molecules have not been reported. Related work with sulfur heteroatoms shows interesting parallels but has been oriented predominantly toward the problem of transannular interactions.[10–14]

There is extensive literature on the theoretical work on both COT[1] and the phosphorus heterocycles, with the main focus on mono-λ^5-phosphorins[4] and on cyclophosphazenes.[3] No efforts have been made here to establish a bonding description of the new phosphorus compound on the same level of sophistication, but it is clear that fundamentally there should be very similar characteristics.

Results and Discussion

Treatment of 1,1-bis[(diphenylphosphino)methyl]ethene (1)[15] with equimolar quantities of 3-chloro-2-(chloromethyl)-1-propene in acetonitrile at 40 °C affords the cyclic bis(phosphonium) salt 2, yet only in moderate yield, because high molecular weight oligomers are formed at the same time. However, attack of the two nucleophilic phosphine centers in 1 at the two chloro functions of the propene appears to be greatly facilitated owing to the pseudo-allylic nature of the reagent.

The solubility properties of 2 are typical for cyclic phosphonium salts. Identification of the product through detailed NMR investigations, as well as through field desorption mass spectrometry and elemental analysis, presented no problem (Experimental Section, Scheme I).

The reaction of compound 2 with 2 equiv of potassium 2-methyl-2-propanolate in tetrahydrofuran at ambient temperature leads to a deep yellow color of the slurry, indicating rapid ylide formation. Already after 1 h a yield

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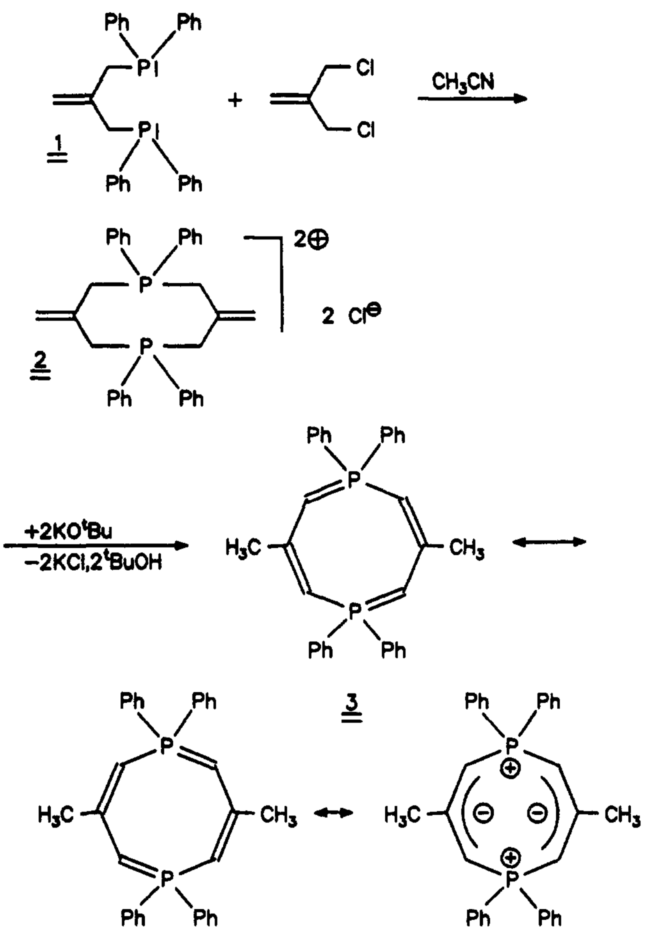
Scheme I



of greater than 90% of an orange-red product **3** is recovered through evaporation of 2-methyl-2-propanol and solvent, and extraction of the product with diethyl ether (Scheme I).

Compound **3** is readily soluble in aromatic hydrocarbons and tetrahydrofuran, more sparingly soluble in diethyl ether. On cooling of the ether solution to −25 °C, orange crystals separate which contain solvent of crystallization according to the X-ray crystal structure investigation (below). The solvent can be removed from the crystals in vacuo to leave ether-free samples.

The composition of the product is confirmed by elemental analysis and electron impact mass spectrometry (Experimental Section). The fully symmetrical structure, not immediately obvious from the constitution of the precursor **2**, could be elucidated through a detailed NMR analysis and an X-ray crystal structural study.

Benzene solutions of compound **3** show a single resonance line in the $^{31}P\{^{1}H\}$ NMR spectrum. The chemical shift $\delta = 1.45$ (ppm) relative to external aqueous H_3PO_4 represents an upfield shift of 20 ppm as compared to the phosphonium precursor **2**, quite typical for a pair of a phosphonium salt and the corresponding phosphonium ylide.[5a] The ^{1}H and ^{13}C NMR spectra contain only one set of phenyl resonances (para, meta, ortho, ipso), which suggests complete equivalence of the four aryl groups of the molecule in solution, and the shifts and multiplicities of the ^{1}H and ^{13}C signals of the four P*CH*C groups in turn indicate equivalence of these moieties. Their chemical shifts and coupling constants are as expected for the allylic functions, i.e. sp^{2}-hybridized carbon atoms bearing a partial negative charge. As for **2**, the ^{13}C resonances for **3** appear as second-order multiplets of the AXX′ type of spin systems owing to a non-zero P–P′ coupling. In the Experimental Section the observed signals are assigned accordingly pseudodoublets or -triplets, respectively, with $N = J(AX) - J(AX')$ referring to the spacing of the high-intensity signals.

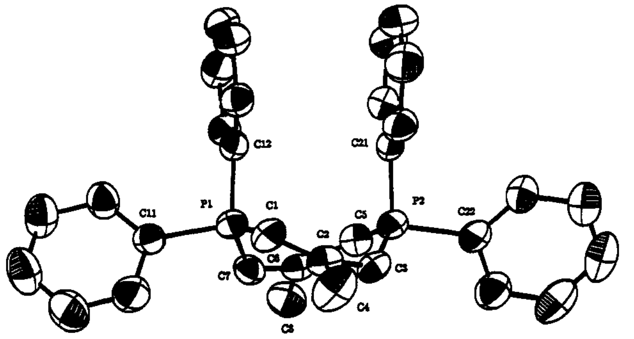


Figure 1. Molecular structure of **3** with the atom-numbering scheme (ORTEP, 50%). (Probability ellipsoids are shown for the heavier atoms; hydrogen atoms are omitted.)

The spectroscopic identification of the *methyl* groups is of prime importance for the assignment of the structure, because these groups are indicative of the postulated proton-transfer rearrangement following the two-step deprotonation of the bis(phosphonium) dication by base (Scheme I). The conversion of the *exo*-methylene groups into methyl groups is obvious from the high-field shift of the H and C signals, as well as from the multiplicity of these resonances. Taken together, the NMR data suggest a virtual D_{2h} point group symmetry for the molecular skeleton in solution on the NMR time scale.

Final proof for such a cyclic bis(phosphonia)–bis(methallylide) structure was provided by the X-ray work. Compound **3** crystallizes in the monoclinic space group $C2/c$ (No. 15) with one molecule of the heterocycle and half a molecule of diethyl ether in the asymmetric unit. The molecule **3** has no crystallographic symmetry, but the structure closely approaches point group C_2, or even C_{2v} (Figure 1). The mesocycle can be described as to have a slightly puckered tub conformation or, when turned upside down, as a vaulted domelike configuration. There are two planar methallylic groups with the central carbon atoms as their center atoms, respectively, which both have a sum of valence angles of exactly 360.0°. The planes of these methallylic groups are twisted relative to each other by 46.06°. The four allylic bonds are very short with an average value of 1.378 (6) Å, in contrast to the two exocyclic bonds C–CH_3 (average 1.515 (3) Å). The four short endocyclic P–C bonds (average 1.732 (5) Å) indicate ylidic character of these bonds, as already deduced from the NMR data. The much longer P–C_{aryl} distances provide reliable internal reference data for this interpretation (Table I).

The folding of the eight-membered ring observed in the solid state would suggest that the phenyl groups are nonequivalent at each phosphorus atom. The NMR data show, however, that in solution rapid inversion is possible which renders the phenyl groups equivalent.

Theoretical calculations on phosphazenes and related compounds, on various levels of sophistication, have consistently shown that tetracoordinate λ^5-phosphorus centers are conjugation barriers for π-systems owing to nodal planes of the σ or d functions employed.[16] Therefore the experimental findings of this study—planar π-methallylic

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Table I. Crystallographic Data for 3

formula	$C_{32}H_{30}P_2(\cdot 0.5Et_2O)$
fw	476.54
cryst syst	monoclinic
space group	*C*2/*c* (No. 15)
a, Å	25.003 (4)
b, Å	16.773 (1)
c, Å	15.614 (2)
α, deg	90
β, deg	116.781 (6)
γ, deg	90
V, $Å^3$	5845.74
Z	8
d_{calc}, g cm^{-3}	1.18
μ(Mo Kα), Å	1.33
F(000), e	2184
temp, °C	20
diffractometer	Enraf-Nonius CAD4
λ (Mo Kα radiation, graphite monochromated), Å	0.71069
scan method	ω
$((\sin\theta)/\lambda)_{max}$, $Å^{-1}$	0.595
hkl range	±26,+19,+18
no. of unique data, total	5147, 5512
no. of obsd data ($F_o > 4\sigma(F_o)$)	4183
structure solution	direct methods
H atoms (found/calc)	33/0
no. of params refined	439
R^a	0.0456
$R_w{}^b$	0.0376
largest shift/esd, final cycle	0.001
$\Delta\rho_{fin}$(max,min), e $Å^{-3}$	0.33, −0.26

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$; $w = 1/\sigma^2(F_o)$. Function minimized: $\sum w(|F_o| - |F_c|)^2$.

parts separated by phosphonium centers, with strong deviations of the overall geometry from planarity, and inversion flexibility of the ring—are in very good agreement with these theoretical models. Recent work on coordination compounds of related $1\lambda^5,3\lambda^5$-diphosphorins[7] has shown that in fact the methallyl parts of the heterocycles are the electron-donating realms where transition-metal atoms become η^3-bound as four-electron acceptors. We expect the title compound to be a good 2 × 4 electron donor ligand, e.g. for bimetallic units. Work to test this concept is in progress.

Experimental Section

All manipulations were performed under an atmosphere of pure dry nitrogen by using standard Schlenk techniques. Solvents were appropriately dried and distilled in an inert-atmosphere prior to use. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were obtained on a JEOL GX400 spectrometer, with the deuterated solvents as internal and 85% H_3PO_4 (δ 0.00) as external standards. Mass spectra were recorded on a MAT 311A (Varian) instrument. Microanalyses were performed at the Analytical Laboratory of this institute.

3,7-Dimethylidene-1,1,5,5-tetraphenyl-1,5-diphosphocanium Dichloride (2). A suspension of 1 (4.80 g, 11.31 mmol) in 70 mL of acetonitrile was treated at 20 °C with a solution of 3-chloro-2-(chloromethyl)-1-propene (1.41 g, 11.31 mmol) in 20 mL of acetonitrile. The reaction mixture was stirred at 40 °C for 3 days. After cooling to room temperature, the white precipitate was filtered and dried in vacuo, yield 1.30 g (20%) of white powder, mp 241 °C. ^1H NMR ($CDCl_3$): δ (ppm) 4.82 (d, ^2J(PH) = 17.58 Hz, 8 H, CH_2P), 5.37 (t, ^4J(PH) = 3.66 Hz, 4 H, $H_2C{=}$), 7.71–7.76 (complex multiplet, total 12 H, *m*/*p*-C_6H_5), 8.04–8.12 (multiplet, ^3J(PH) = 12.08 Hz, 8 H, *o*-C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 28.98 (d, ^1J(PC) = 50.38 Hz, CH_2P), 117.97 (pseudodoublet, *N* = 85.1 Hz, C_{ipso}, AXX′), 124.99 (t, ^3J(PC) = 9.05 Hz, $CH_2{=}$), 129.63 (t, ^2J(PC) = 11.49 Hz, $C{=}CH_2$), 130.64 (pseudotriplet, *N* = 6.3 Hz, C_{ortho}, AXX′), 133.35 (pseudotriplet, *N* = 4.9 Hz, C_{meta}, AXX′), 135.29 (s, C_{para}). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 21.75 (s). MS (*m*/*e*, FD): 477.3 ($M - H^+$). Anal. Calcd for $C_{32}H_{32}P_2Cl_2$: C, 69.95; H, 5.87; P, 11.27; Cl, 12.90. Found: C, 69.96; H, 6.05; P, 11.59; Cl, 12.62.

Table II. Positional Parameters, Equivalent Isotropic Thermal Parameters, and Their Estimated Standard Deviations for 3[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq), $Å^2$
P(1)	0.20481 (3)	0.81757 (4)	0.17084 (4)	0.036
P(2)	0.33582 (3)	0.86344 (4)	0.37608 (4)	0.034
C(1)	0.2648 (1)	0.8068 (2)	0.1447 (2)	0.038
C(2)	0.3185 (1)	0.8475 (1)	0.1859 (2)	0.042
C(3)	0.3457 (1)	0.8830 (1)	0.2752 (2)	0.031
C(4)	0.3524 (1)	0.8533 (2)	0.1265 (2)	0.049
C(5)	0.2769 (1)	0.9078 (1)	0.3880 (2)	0.042
C(6)	0.2233 (1)	0.9323 (1)	0.3149 (2)	0.034
C(7)	0.1966 (1)	0.9063 (1)	0.2210 (2)	0.043
C(8)	0.1898 (2)	0.9963 (2)	0.3399 (3)	0.060
C(11)	0.1383 (1)	0.8129 (1)	0.0554 (2)	0.041
C(111)	0.0907 (1)	0.7625 (2)	0.0369 (2)	0.050
C(112)	0.0395 (1)	0.7656 (2)	−0.0488 (2)	0.058
C(113)	0.0349 (2)	0.8197 (2)	−0.1177 (2)	0.080
C(114)	0.0821 (2)	0.8683 (2)	−0.1022 (2)	0.075
C(115)	0.1335 (2)	0.8647 (2)	−0.0169 (2)	0.050
C(12)	0.1949 (1)	0.7329 (1)	0.2347 (2)	0.033
C(121)	0.1623 (1)	0.7397 (2)	0.2859 (2)	0.039
C(122)	0.1493 (1)	0.6727 (2)	0.3252 (2)	0.043
C(123)	0.1689 (1)	0.5989 (2)	0.3124 (2)	0.042
C(124)	0.2018 (1)	0.5917 (2)	0.2623 (2)	0.051
C(125)	0.2147 (1)	0.6583 (1)	0.2236 (2)	0.043
C(21)	0.3395 (1)	0.7565 (1)	0.3965 (2)	0.034
C(211)	0.3710 (1)	0.7071 (2)	0.3651 (2)	0.046
C(212)	0.3782 (2)	0.6272 (2)	0.3916 (3)	0.065
C(213)	0.3537 (2)	0.5982 (2)	0.4486 (3)	0.059
C(214)	0.3218 (1)	0.6466 (2)	0.4789 (2)	0.050
C(215)	0.3145 (1)	0.7258 (2)	0.4528 (2)	0.039
C(22)	0.4021 (1)	0.9015 (1)	0.4778 (2)	0.034
C(221)	0.4467 (1)	0.8525 (2)	0.5421 (2)	0.044
C(222)	0.4957 (1)	0.8836 (2)	0.6190 (2)	0.058
C(223)	0.5015 (2)	0.9641 (3)	0.6321 (2)	0.048
C(224)	0.4585 (2)	1.0141 (2)	0.5694 (3)	0.043
C(225)	0.4085 (1)	0.9833 (2)	0.4920 (2)	0.047

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameters, *U*(eq), defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor; $U(eq) = {}^1/_2 \sum_i\sum_j U_{ij}\, a_i{}^*a_j{}^*\, \mathbf{a}_i\mathbf{a}_j$.

Table III. Selected Bond Distances (Å) and Angles (deg) for 3[a]

Distances			
P(1)–C(1)	1.732 (2)	P(2)–C(3)	1.731 (2)
P(1)–C(7)	1.735 (2)	P(2)–C(5)	1.734 (2)
C(2)–C(1)	1.380 (3)	C(2)–C(3)	1.381 (3)
C(6)–C(7)	1.380 (3)	C(6)–C(5)	1.375 (3)
C(2)–C(4)	1.515 (3)	C(6)–C(8)	1.515 (3)
P(1)–C(11)	1.822 (2)	P(2)–C(21)	1.817 (2)
P(1)–C(12)	1.815 (2)	P(2)–C(22)	1.818 (2)
Angles			
P(1)–C(1)–C(2)	127.1 (2)	P(2)–C(3)–C(2)	129.1 (2)
P(1)–C(7)–C(6)	130.7 (2)	P(2)–C(5)–C(6)	126.6 (2)
C(1)–C(2)–C(3)	128.0 (2)	C(5)–C(6)–C(7)	127.6 (2)
C(1)–C(2)–C(4)	116.2 (2)	C(5)–C(6)–C(8)	116.3 (2)
C(3)–C(2)–C(4)	115.8 (2)	C(7)–C(6)–C(8)	116.1 (2)
C(1)–P(1)–C(7)	119.1 (1)	C(3)–P(2)–C(5)	119.5 (1)
C(1)–P(1)–C(11)	105.3 (1)	C(3)–P(2)–C(21)	109.3 (1)
C(1)–P(1)–C(12)	113.2 (1)	C(3)–P(2)–C(22)	106.3 (1)
C(7)–P(1)–C(11)	104.1 (1)	C(5)–P(2)–C(21)	112.5 (1)
C(7)–P(1)–C(12)	110.5 (1)	C(5)–P(2)–C(22)	103.9 (1)
C(11)–P(1)–C(12)	102.7 (1)	C(21)–P(2)–C(22)	103.8 (1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

3,7-Dimethyl-1,1,5,5-tetraphenyl-$1\lambda^5,5\lambda^5$-diphosphocin (3). A suspension of 2 (0.10 g, 0.182 mmol) in 30 mL of tetrahydrofuran was carefully treated with solid potassium 2-methyl-2-propanolate (0.04 g, 0.364 mmol) at 20 °C. The reaction mixture was stirred for 1 h, and it turned slowly to an orange solution. Then tetrahydrofuran and 2-methyl-2-propanol were stripped in in vacuo, the residue was extracted selectively with diethyl ether, and the solution was cooled until crystallization of **3** started (at −25 °C); yield 0.078 g (90%) of orange-yellow crystals, mp 148 °C dec. ^{1}H NMR (C_6D_6): δ (ppm) 2.34 (s, 6 H, CH_3), 3.54 (d, ^2J(PH) = 16.61 Hz, 4 H, PCH), 6.85–6.98 (complex multiplet, total 12 H, *m*/*p*-C_6H_5), 7.38–7.46 (multiplet, ^3J(PH) = 11.60 Hz, 8 H, *o*-C_6H_5). $^{13}C\{^1H\}$ NMR (C_6D_6): δ (ppm) 30.61 (t, ^3J(PC) = 16.63 Hz, CH_3), 62.62 (d × d, ^1J(PC) = 110.72 Hz, ^3J(PC) = 5.38 Hz, PCH), 128.10–128.43 (complex multiplet, C_{meta}, AXX′), 128.92–129.95 (pseudotriplet, C_{para}, AXX′), 132.24–132.44 (complex multiplet, C_{ortho}, AXX′), 135.50 (d × m, ^1J(PC) = 89.5 Hz, C_{ipso}, AXX′), 164.15 (t, ^2J(PC) = 6.85 Hz, *C*–CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ (ppm) 1.45 (s). MS (*m*/*e*, EI): 476 (M^+). Anal. Calcd for $C_{32}H_{30}P_2 \cdot 0.5Et_2O$: C, 78.29; H, 6.76; P, 11.87. Found: C, 78.01; H, 6.24; P, 12.09.

Crystallography. A small part of a cubelike crystal of ether-solvated $C_{32}H_{30}P_2$ was mounted in a glass capillary and directly examined on the diffractometer. Geometric and intensity data were collected with an Enraf-Nonius CAD4 diffractometer. Pertinent crystallographic data are given in Table I. Lattice dimensions and Laue symmetry were determined from reflections $20.1 \le \theta \le 21.6°$. From systematic absences the space group was uniquely determined as *C*2/*c*. Intensity data (ω-scan) showed a significant decrease of 13.7% during the first hours (evaporation of Et_2O until saturation inside the closed capillary was reached) and were reduced by routine procedures.[17] The two phosphorus atoms of the formula unit $C_{32}H_{30}P_2$ were located by direct methods (SHELXS-86),[17] and the remaining parts of the molecule in a series of least squares refinements and difference Fourier maps. The atoms of the solvent diethyl ether molecule (a half molecule in the asymmetric unit with a site occupancy 0.5 for the oxygen atom) were found by an alternating sequence of least squares refinements and difference Fourier maps. All hydrogen atoms (except for those on the slightly disordered diethyl ether molecule) could be found, and nearly all of them were refined isotropically. The methyl group at atom C(2) was found to be disordered over two sites and was refined satisfactorily with two sets of three 0.5 H atoms. This resulted in residuals $R = 0.0456$ and $R_w = 0.0376$ and an excellent difference Fourier map with all peaks well below 1 e Å^{-3}. The atomic positional parameters for the non-hydrogen atoms are listed in Table II. Supplementary material has been deposited.

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Supplementary Material Available: Tables of atomic positions, bond distances, interbond angles, and anisotropic thermal parameters (12 pages); a listing of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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[17] Calculations were done by using a Micro-Vaxstation 3100 M76 (Micro VMS V5.3) computer with the programs SHELXS-86 (structure solution), SHELX-76 (structure refinement), DELOS, LEPAGE (cell reduction), and the commerical package SDP/V V3.0.

Synthesis and Molecular Structure of a Dinuclear Ruthenium Dihydride Complex Containing a Perpendicularly Bridging Diphenylacetylene Ligand

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Summary: The reaction of a dinuclear tetrahydridoruthenium complex $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_4Ru(\eta^5\text{-}C_5Me_5)$ (**1**) with 2 equiv of diphenylacetylene results in the formation of the dinuclear ruthenium dihydride complex $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_2(\mu\text{-}PhCCPh)Ru(\eta^5\text{-}C_5Me_5)$ (**2**), which contains a perpendicularly bridging diphenylacetylene ligand. The complex crystallizes in the triclinic system, in space group $P\bar{1}$, with $a = 10.284$ (4) Å, $b = 15.871$ (4) Å, $c = 10.286$ (3) Å, $\alpha = 98.47$ (3)°, $\beta = 110.92$ (2)°, $\alpha = 98.22$ (3)°, $V = 1515.8$ (9) Å^3, and $Z = 2$. Anisotropic refinement of all atoms except hydrogen atoms converged to the residuals $R = 0.0569$ and $R_w = 0.0539$ for 6177 reflections.

Transition-metal polyhydride complexes have the potential for creating coordinative unsaturation by thermal induced or photoinduced reductive elimination of dihydrogen.[1] The coordination sites are also generated upon reaction of polyhydride complexes with olefins. In such reactions, bulky, poorly coordinating, metalation-resistant olefin is used as a hydrogen acceptor. Crabtree et al. reported the dehydrogenation of cyclic alkanes by an Ir(III) complex in the presence of *tert*-butylethylene as a hydrogen acceptor.[2] Similar reactions involving Re(VII) complexes were discovered by Felkin and co-workers.[3]

In the preceding communication, we reported that a dinuclear ruthenium tetrahydride-bridged complex, $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_4Ru(\eta^5\text{-}C_5Me_5)$,[4] reacted with ethylene to afford a dinuclear divinyl complex, $(\eta^5\text{-}C_5Me_5)Ru(CH{=}CH_2)_2(CH_2{=}CH_2)Ru(\eta^5\text{-}C_5Me_5)$, via an activation of the C(sp^2)–H bond of ethylene.[5] In the early stage of this reaction, the ethylene molecule accepted two hydrogen

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