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ARTICLE

Versatile Reactivity of Cyclic 1,2-Dimethylhydrazinodiphosphines

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Dedicated to Professor Evamarie Hey-Hawkins on the Occasion of her 60th Birthday

Abstract. A versatile reactivity from the cage compound $P(NMeNMe)_3P$ is presented. The Staudinger reaction with Me_3SiN_3 is carried out. The crystal structure of the compound issued from the reaction on both sides ($Me_3SiN{=}P(NMeNMe)_3P{=}NSiMe_3$) is reported. When the reaction occurs on only one side, the remaining free phosphorus atom is complexed with $RuCl_2$(*p*-cymene). $P(NMeNMe)_3P$ reacts with PCl_3, leading to the heterocyclic compound $ClP(NMeNMe)_2PCl$. This heterocycle also displays a versatile reactivity. Substitution reaction with $HNiPr_2$ leads to $iPr_2NP(NMeNMe)_2PNiPr_2$. Very complex ^1H and ^{13}C NMR spectra suggest that the *cis* isomer is the largely major isomer of this compound. The *cis* structure is confirmed by X-ray diffraction. Besides the reaction on the P–Cl functions, the reaction on the lone pair of $ClP(NMeNMe)_2PCl$ is carried out, leading to the complex (*p*-cymene)$Cl_2RuPCl(NMeNMe)_2ClPRuCl_2$(*p*-cymene). Characterization of this compound by X-ray diffraction displays a *cis* isomer for this compound also.

Introduction

Cage-like phosphorus derivatives possess interesting properties as ligands in homogeneous catalysis.[1] Among them, the cage ligand tris(1,2-dimethylhydrazinodiphosphine) $P(NMeNMe)_3P$ is known since a long time.[2,3] A few symmetrical complexes of $P(NMeNMe)_3P$ have been reported, concerning BH_3,[2,4–6] $W(CO)_5$ and $Ni(CO)_3$,[7,8] $Fe(CO)_4$,[9] and $Al(Et)_3$.[10] However, this ligand has not generated a wide attention for decades, until its first use as ligand for catalysis, in the Karash addition of bromotrichloromethane to olefins.[11] Recent developments of this cage compound concern the catalyzed selective hydration of nitriles to amides in aqueous medium, using either Ru[12,13] or Rh[14] complexes of $P(NMeNMe)_3P$.

In the context of the recent interest in this cage compound as ligand for catalysis, we wish to report herein that a versatile reactivity can be carried out from this compound, including complexation experiments, but not only.

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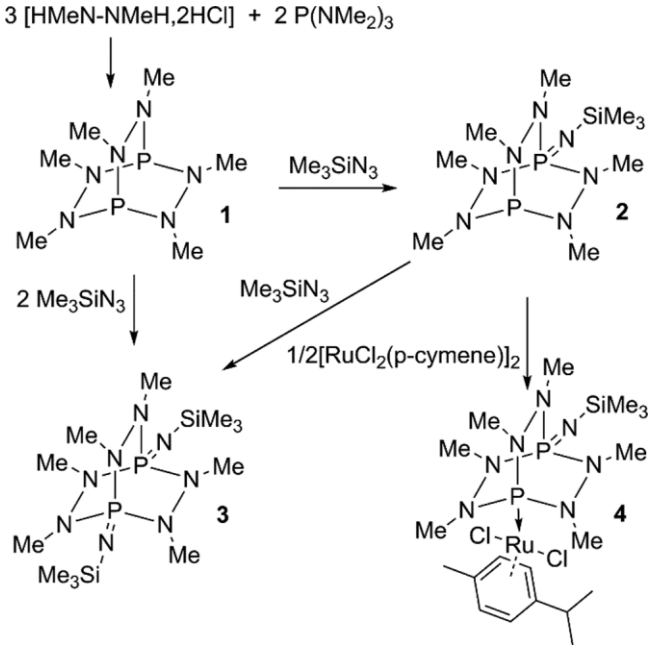
Results and Discussion

The cage compound $P(NMeNMe)_3P$ (**1**) was synthesized by heating 3 equiv. of *N*,*N*′-dimethylhydrazine dihydrochloride with 2 equiv. of tris(dimethylaminophosphine), as previously reported.[2] However, we slightly modified this method, by using toluene instead of benzene, and the prior extraction with pentane facilitates the sublimation step. Compound **1** is in particular characterized by a singlet in ^{31}P NMR (δ = 108 ppm) and a pseudo triplet with a broad central signal in ^1H NMR (δ = 2.85 ppm).

The Staudinger reaction of compound **1** with trimethylsilyl azide was then attempted (Scheme 1). Previous work reported a straightforward reaction with a few azides, in particular with PhN_3,[15–17] $Ph_2P(O)N_3$,[7,15,16] and $(PhO)_2P(O)N_3$.[7,16] We have also reported that in the case of the azide $N_3(CH_2)_3NH_2$, reaction on only one or on both phosphorus atoms occurred.[18] Unexpectedly, the reaction of the cage compound **1** with Me_3SiN_3 never went to completion, even after 5 weeks at 70 °C, with addition of two additional equiv. of azide each week. The reaction was monitored by ^{31}P NMR, which displayed first, besides the singlet of the starting compound **1** (δ = 108 ppm) the presence of two doublets at δ = +95 (P^{III}) and –4 (P=N) ppm ($^3J_{PP}$ = 79 Hz), corresponding to the reaction on a single phosphorus atom (compound **2** in Scheme 1). These values compare well with those obtained for the single reaction with the azide $N_3(CH_2)_3NH_2$ (δ = 95 and 3 ppm, $^3J_{PP}$ = 75 Hz).[18] Continuing the reaction induces the appearance of another singlet at δ = –7 ppm, which corresponds to the reaction on both sides of compound **1**, to afford compound **3**. Compounds **2** and **3** are isolated by fractional distillation under reduced pressure.

Colorless single crystals of compound **3** could be isolated, and analyzed by X-ray diffraction. Crystallographic data and



Scheme 1. Synthesis and versatile reactivity from the cage compound **1**.

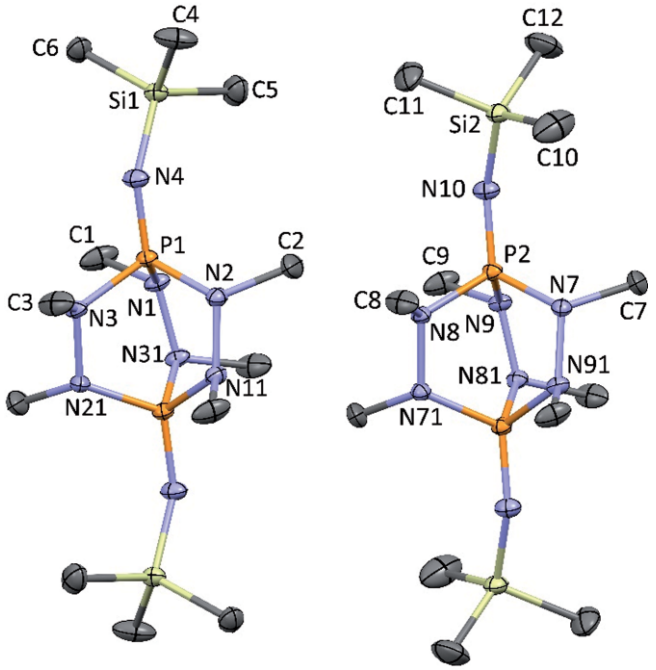


Figure 1. Crystal structure of compound **3** (two half molecules per asymmetric unit with 50 % probability each). Selected bond lengths /Å and angles /°: P1–N1 1.676(2), P1–N11 1.650(2), P1–N2 1.657(2), P1–N21 1.693(2), P1–N3 1.684(2), P1–N31 1.680(2), P1–N4 1.5115(11), P2–N7 1.660(2), P2–N71 1.7005(19), P2–N8 1.667(2), P2–N81 1.679(2), P2–N9 1.644(2), P2–N91 1.691(2), P2–N10 1.5116(11), P1···P1^{i} = 2.8812(4), P2···P2^{ii} = 2.8735(4). Si1–N4–P1 145.69(6), Si2–N10–P2 149.64(6).

details of the crystal structure refinement are given in Table 1. As shown in Figure 1, which displays the crystal structure of compound **3**, two forms with 50 % probability each are observed. These forms differ by the different orientation of the N–Me groups of the cage. An analogous disorder was previously observed in the crystal structure of the cage compound

Table 1. Crystallographic data and details of the crystal structure refinement for compounds **3**, **6**, and **7**.

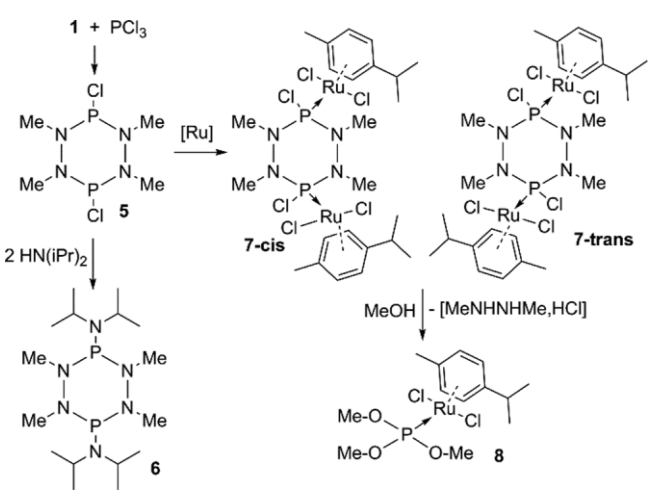
	3	**6**	**7**
Molecular formula	$C_{12}H_{36}N_8P_2Si_2$	$C_{16}H_{40}N_6P_2$	$C_{24}H_{40}Cl_6N_4P_2Ru_2,(H_2O)_5$
Molecular weight	410.59	378.48	951.49
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P1\ 2_1/n1$	$P1\ 2_1/n1$
a /Å	7.1476(4)	10.3389(9)	13.6587(12)
b /Å	13.0843(9)	17.4420(15)	23.9424(19)
c /Å	13.2770(9)	12.9102(9)	13.8556(11)
α /°	69.661(6)	90	90
β /°	83.497(5)	99.863(9)	110.451(8)
γ /°	90.886(5)	90	90
Cell volume /Å^3	1154.77(14)	2293.7(3)	4245.5(6)
Z	2	4	4
Calcd density	1.18	1.096	1.489
μ /mm^{-1}	0.304	0.200	1.198
Crystal size /mm	0.15 × 0.35 × 0.42	0.15 × 0.30 × 040	0.10 × 0.10 × 0.15
Diffractometer	XCALIBUR	Stoe IPDS	XCALIBUR
T /K	180	180	180
θ range /°	3–29	2–26	3–29
Reflections collected	10656	22750	40079
Reflections unique	6114	4249	11342
R_{int}	0.028	0.105	0.097
Reflections with $I > n\sigma(I)$	4555 (n = 3.00)	2173 (n = 0.9)	3719 (n = 2.2)
Parameters refined	271	217	363
R [$I > n\sigma(I)$]	0.0425	0.0534	0.0760
R_w[$I > n\sigma(I)$]	0.0396	0.0590	0.0754
GooF (F)	1.163	1.064	1.102
$\Delta\rho_{max}/\Delta\rho_{min}$ /e•Å^{-3}	0.35/–/-0.31	0.31/–/-0.33	2.82/–/-1.39

1,[19] but also for the dioxide of **1** [O=P(NMeNMe)$_3$P=O].[20] The average bond length for the phosphorus nitrogen bonds is 1.67 Å for the single bonds, with a large variability from 1.644(2) to 1.7005(19) Å, and 1.51 Å for the double bonds. These values are in the range found for other phosphorus heterocycles including N–N–P–N–N linkages.[21] The angle around the nitrogen atom in the P=N–Si linkages is 145.19(9)° for one form, 148.24(9)° for the other form. The intramolecular distance between both phosphorus atoms is 2.8812(4) Å for P1···P1^i, and 2.8735(4) Å for P2···P2^i. The dihedral angles N4–P1···P1i–N4i and N10–P2···P2i–N10i are 180°.

The unsymmetrical cage compound **2** is interesting, as the unreacted phosphorus can be used for further functionalization, for instance for the complexation with ruthenium. The reaction with [RuCl$_2$(*p*-cymene)]$_2$ induces a deshielding of the signal corresponding to the P^{III} atom from δ = 95 ppm in compound **2** to 116.4 in the complex **4**. The value of the coupling constant $^3J_{PP}$ increases from 79 Hz to 97 Hz. Compound **4** was also tentatively synthesized by adding first one equivalent of Ru to compound **1**, then reacting the azide on the remaining phosphorus. However, this alternative route to compound **4** was unsuccessful. Indeed, the complexation on a single phosphorus of compound **1** is not stable, and a disproportionation is observed with time, leading to a mixture of unreacted **1** and of the double Ru complex of **1**, already synthesized and characterized by X-ray diffraction.[11]

Besides the reactions on the lone pair of the phosphorus atoms, it has been shown previously that the cage compound **1** reacts with PCl$_3$, leading quantitatively to the heterocyclic derivative **5**.[2] In view of the proposed mechanism of this reaction,[22] a "*cis*" arrangement for the P–Cl functions is expected to be the largely major isomer of compound **5**, but surprisingly, the published crystal structure of compound **5** displayed a "*trans*" arrangement for both P–Cl functions.[23] A single singlet is observed by ^{31}P NMR for compound **5**, at δ = 120.3 ppm, as previously reported.[22] A versatile reactivity can be developed from this compound **5**, around the phosphorus atoms, on the P–Cl functions, or on the lone pairs of phosphorus. Reaction of compound **5** with two equivalents of diisopropylamine affords compound **6** (Scheme 2). The reaction is monitored by ^{31}P NMR, which displays the presence of a single singlet at δ = 112.8 ppm for compound **6**, instead of 120.3 ppm for **5**.

Unexpectedly, the ^{1}H NMR spectrum of compound **6** is very complex. Four doublets with a same intensity are observed for the methyl groups of the N*i*Pr$_2$ functions, two doublets for the NMe groups with a different coupling constant with phosphorus (δ = 2.64, $^3J_{HP}$ = 7.8 Hz; 2.80, $^3J_{HP}$ = 12.8 Hz), and two very different multiplets for the H of the N*i*Pr$_2$ groups (δ = 3.20 and 4.69 ppm). ^{31}P decoupling, and COSY experiments were carried out (see Supporting Information). The CH signal at δ = 3.20 ppm correlates with two of the doublets of the *i*Pr groups (δ = 1.17 and 1.26 ppm), whereas the CH signal at δ = 4.69 ppm correlates with the two other doublets of the *i*Pr groups (δ = 0.97 and 1.10 ppm). The ^{13}C{^{1}H} {^{31}P} NMR is also more complex than expected, with two broad singlets for the methyl groups of the *i*Pr groups (δ = 20.91 and 22.08 ppm), two different singlets for the CH of the *i*Pr groups (δ = 43.16 and 45.22 ppm), and two very different singlets for the NMe groups (δ = 26.25 and 34.16 ppm). The complexity of the ^{1}H and ^{13}C NMR spectra is poorly compatible with a "*trans*" arrangement of the N*i*Pr$_2$ groups. Indeed, a "*cis*" arrangement should induce some difficulties for the free rotation of the substituents, and thus may account for the complexity of the NMR spectra. In order to ascertain this "*cis*" arrangement, colorless single crystals of compound **6** suitable for X-ray diffraction were obtained. The results are shown in Figure 2 and the data are listed in Table 1. As expected from the NMR spectroscopic data, compound **6** displays a "*cis*" arrangement of the N*i*Pr$_2$ groups [the dihedral angle N5–P1···P2–N6 is 22.93(16)°]. Two different arrangements of the NMe groups are also observed in the crystal structure, corroborating the results of ^{1}H and ^{13}C NMR spectroscopy. The sum of angles around the phosphorus atoms is 301.66° for P1 and 301.76° for P2. Figure 3 displays the view of the crystal structure of compound **6**, with the superimposition of the P atoms, showing the very unsymmetri-



Scheme 2. Synthesis and versatile reactivity from the heterocyclic compound **5**. [Ru] = [RuCl$_2$(*p*-cymene)]$_2$.

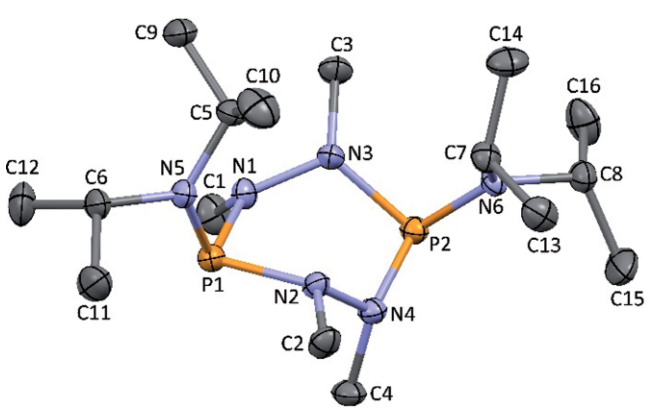


Figure 2. Crystal structure of compound **6**. Selected bond lengths /Å and angles /°: N1–P1 1.697(3), N2–P1 1.739(3), N5–P1 1.662(3), N3–P2 1.740(2), N4–P2 1.702(3), N6–P2 1.667(3), P1···P2 = 3.510(2); N1–P1–N2 94.63(12), N2–P1–N5 99.22(13), N1–P1–N5 107.79(15), N3–P2–N4 94.79(14), N3–P2–N6 98.85(13), N4–P2–N6 108.15(13).

cal nature of this compound, and the easy access to the phosphines on one side.

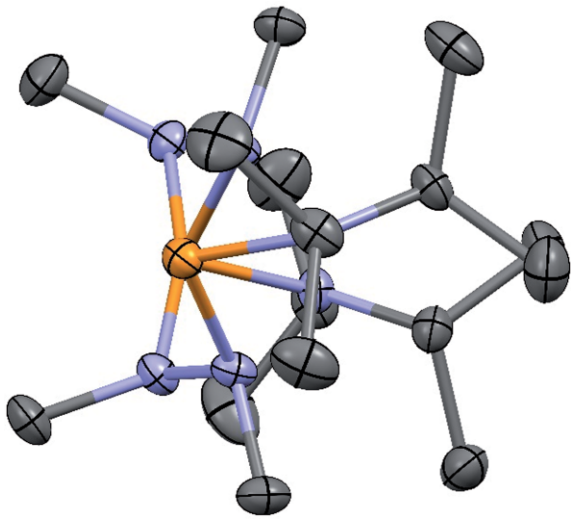


Figure 3. Another view of the crystal structure of compound **6**, with superimposition of the phosphorus atoms.

Another possibility of reaction of compound **5** is the complexation of the lone pair of the phosphorus atoms. As we have shown in Scheme 1 the reaction with $[RuCl_2(p\text{-cymene})]_2$, the analogous reaction was attempted with compound **5** (Scheme 2). The complexation was monitored by ^{31}P NMR, which displayed the disappearance of the singlet corresponding to compound **5** (δ = 120.3 ppm) and the appearance of two close singlets at δ = 165.5 (major, ca. 83 %) and 164.3 (minor, ca. 17 %) ppm, corresponding to the complex **7**. This ratio is exactly the one that is expected for *cis* and *trans* isomers, but not detected, for the synthesis of compound **5** from the cage compound **1**. Thus the complexation with ruthenium allows differentiating the **7-cis** (major isomer) and the **7-trans** (minor isomer) complex (Scheme 2). The presence of both isomers is also detected by ^{1}H and ^{13}C NMR spectroscopy. Some signals corresponding to the minor isomer are indicated with an asterisk (*) in the Experimental Section, but several of them are hidden under the signals of the major isomer. The steric hindrance in compound **7-cis** is also high, as two different NMe groups are observed in ^{1}H NMR, as already seen for compound **6**. The presence of *cis* and *trans* isomers has been already documented for other six-membered heterocycles including two phosphines, such as 1,4,2,5-diazadiphosphorinanes.[24]

Single crystals of **7** were grown from the major isomer, thus its structure could be determined by X-ray crystallography (Figure 4, and Table 1). As expected from the NMR spectroscopic data, a "*cis*" arrangement is observed. The dihedral angle Ru1–P1···P2–Ru2 is 20.11(68)°, and Cl1–P1···P2–Cl2 is 24.58(27)°. The sum of angles around the phosphorus atoms (excluding Ru) is 299.8° for P1 and 302° for P2, very close to what was obtained for compound **6** (301.66° for P1 and 301.76° for P2).

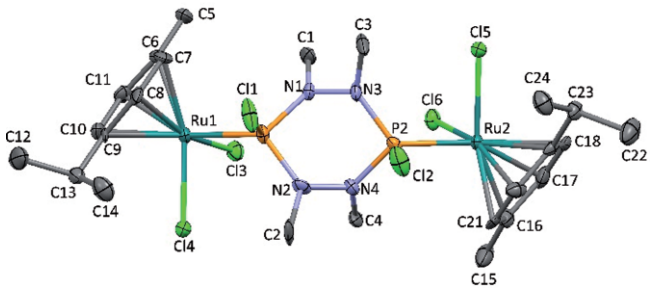


Figure 4. Crystal structure of compound **7-cis**. Selected bond lengths /Å and angles /°: P1–N1 1.655(11), P1–N2 1.665(12), P2–N3 1.645(12), P2–N4 1.639(11), P1–Cl1 2.085(5), P2–Cl2 2.097(5), Ru1–P1 2.282(3), Ru2–P2 2.294(4), P1···P2 2.357(7); N1–P1–N2 97.9(6), N1–P1–Cl1 102.8(4), N2–P1–Cl1 99.1(5), N3–P2–N4 99.7(6), N3–P2–Cl2 98.4(5), N4–P2–Cl2 103.9(5). Five water molecules associated to the structure are not shown.

In view of the X-ray structure of compound **7**, the P–Cl groups are easily accessible, and thus should be used for further reactions. The reaction with methanol was attempted, and monitored by ^{31}P NMR spectroscopy. An intermediate signal at δ = 131 ppm was observed, which might correspond to the expected reaction on the P–Cl functions, but, the final (isolated) product of the reaction with methanol is characterized by a singlet at δ = 118.3 ppm. Surprisingly, the ^{1}H NMR spectrum of this compound (**8**) displays the total disappearance of the signals corresponding to the NMe groups, showing that the cyclic structure is broken. In contrast, all the signals of the *p*-cymene group are still present, showing that the complexation of phosphorus with Ru still exists. Besides the signals for the *p*-cymene group, the sole other signal in ^{1}H NMR is a doublet (δ = 3.78, $^{3}J_{HP}$ = 11.1 Hz), with an integration of three relative to the *p*-cymene group. Based on these data, the structure of compound **8** should be $(MeO)_3PRuCl_2(p\text{-cymene})$. This compound was already synthesized,[25] and the ^{31}P, ^{1}H, and ^{13}C NMR spectra are identical to those of compound **8**. The mechanism leading to the synthesis of compound **8** is presumably first the reaction of MeOH on the P–Cl functions, leading to the expected P–OMe functions, with generation of HCl, which is trapped by one nitrogen of the heterocycle. The presence of an ammonium close to phosphorus should induce the cleavage of the P–N bond, and regenerate a P–Cl bond, which can further react with MeOH, and so on, up to the full cleavage of all P–N bonds.

Conclusions

We have described in this paper several new derivatives of the cage compound $P(NMeNMe)_3P$ (**1**), using Staudinger reactions, complexations, and substitution reactions. Three of them were characterized by X-ray diffraction. Several of these new compounds could be useful in the future. Indeed, the potential cleavage of the N–$SiMe_3$ groups might afford graftable catalysts (from compound **4**), or polymers (from compound **3**). A careful substitution on the P–Cl groups of compound **7** may afford a family of catalysts, and the easily accessible free phosphines in compound **6** could be used as a pincer ligand.

Experimental Section

General: The reagents and solvents were bought from Aldrich, Acros Organics, and Strem. Solvents were distilled prior use: toluene over sodium, pentane over phosphorus pentoxide. NMR spectra were collected with Bruker AV 300 and AV 500 spectrometers. The reference for ^{1}H and ^{13}C NMR is $SiMe_4$; the reference for ^{31}P NMR is H_3PO_4 (85 % in water). Melting points were determined with an Electrothermal digital melting point apparatus and are uncorrected. Mass spectra were recorded with LC/MSD-TOF (Agilent technologies), Thermo Fisher DS QII, or Neromag R10–10. Compound **1** was synthesized by a method derived from a published procedure.[2]

Synthesis of the Tris(1,2-dimethylhydrazinodiphosphine) (1): A mixture of *N*,*N*′-dimethylhydrazine dihydrochloride (10 g, 75.18 mmol) and hexamethyltriamidophosphite (8.38 g, 51.37 mmol) in toluene (200 mL) was refluxed with stirring for 3 d. The reaction mixture was evaporated to dryness under vacuum, then dry pentane (150 mL) was added, and the mixture was leaved to be vigorously stirred overnight. The precipitate was filtered away and the solution was evaporated to dryness. The resulting solid was carefully extracted three times with dry pentane (3 × 50 mL). The pentane extracts were collected and the solvents evaporated to dryness under vacuum. The product was further purified by sublimation in vacuo. Yield 4.83 g (82 %): **$^{31}P\{^{1}H\}$ NMR** ($CDCl_3$): δ = 108 (s) ppm. **^{1}H NMR** ($CDCl_3$): δ = 2.85 ("t", $^{3}J_{HP}$ = 7.7 Hz, CH_3) ppm.

Synthesis of the Cage Compounds 2 and 3: To a solution of compound **1** (900 mg, 3.81 mmol) in dry toluene (5 mL), trimethylsilylazide (3 mL, 22.86 mmol) was added. The reaction was heated at 70 °C for 5 weeks. After every weak trimethylsilylazide (3 mL, 22.86 mmol) was added to the reaction mixture. Afterwards, the reaction mixture was evaporated to dryness, and the product was extracted with pentane. The resulting solution was evaporated to dryness. Compound **2** was isolated by sublimation, and compound **3** was purified by distillation with a Büchi oven (250 °C, 10 Torr). Compound **2**: **$^{31}P\{^{1}H\}$ NMR** (CD_2Cl_2): δ = 95.1 (d, $^{3}J_{PP}$ = 79 Hz, P^{III}), –4.6 (d, $^{3}J_{PP}$ = 79 Hz, P=N) ppm. **^{1}H NMR** (CD_2Cl_2): δ = 0.047 (s, 9 H, Si-Me), 2.85–2.73 (m, 18 H, N-Me) ppm. Compound **3**: Yield 725 mg (46 %). Colorless crystals. M. p. = 143–145 °C. **$^{31}P\{^{1}H\}$ NMR** ($CDCl_3$): δ = –7.0 (s) ppm. **^{1}H NMR** (CD_2Cl_2): δ = 0.07 (s, 18 H, Si-Me), 2.83 (t, $^{3}J_{HP}$ = 5.7 Hz, 18 H, N-Me) ppm. **$^{13}C\{^{1}H\}$ NMR** (CD_2Cl_2): δ = 3.1 (t, $^{3}J_{CP}$ = 1.5 Hz, C–Si), 36.2 (t, $^{2}J_{CP}$ = 2.8 Hz, C–N) ppm. **ESI-MS** (acetonitrile) *m*/*z*: 411.5 (MH^+, calcd. for $[C_{12}H_{36}N_8P_2Si_2+H]^+$ 411.2). $C_{12}H_{36}N_8P_2Si_2$ (410.60): calcd. C 35.10; H 8.84; N 27.29 %; found: C 34.29; H 8.72; N 27.46 %. Colorless single crystals suitable for X-ray diffraction were obtained from the solution of **3** in CD_2Cl_2, in the NMR tube.

Synthesis of the Ru Cage Complex 4: A solution of compound **2** (169 mg, 0.522 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a cold solution (–80 °C) of $[RuCl_2(p\text{-cymene})]_2$ (160 mg, 0.262 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was left to reach room temperature and evaporated to dryness. Washings with pentane induced the elimination of the slight excess of compound **2**, to afford complex **4** as an orange powder. Yield 300 mg (91 %). **$^{31}P\{^{1}H\}$ NMR** ($CDCl_3$): δ = 116.4 (d, $^{3}J_{PP}$ = 97 Hz, P-Ru), –1.5 (d, $^{3}J_{PP}$ = 97 Hz, P = N) ppm. **^{1}H NMR** (CD_2Cl_2): δ = 0.08 (s, 9 H, CH_3Si), 1.36 (d, $^{3}J_{HH}$ = 6.6 Hz, 6 H, *CH*$_3$–CH), 2.23 (s, 3H CH_3–Cym), 2.95 (sept, $^{3}J_{HH}$ = 6.6 Hz, 1 H, CH_3–*CH*), 3.06 (d, $^{3}J_{HP}$ = 11.1 Hz, 9 H, CH_3–N), 3.12 (d, $^{3}J_{HP}$ = 11.7 Hz, 9 H, CH_3–N), 5.51 (m, 2 H, H of Cym), 5.80 (m, 2 H, H of Cym) ppm.

Synthesis of the Bis(1,2-dihydrazinodiphosphine) (5): This compound was synthesized as published.[2] **$^{31}P\{^{1}H\}$ NMR** (CD_2Cl_2): δ = 120.3 (s) ppm. **^{1}H NMR** (CD_2Cl_2): δ = 3.05 (d, $^{3}J_{HP}$ = 17.1 Hz, 12 H, CH_3) ppm. **$^{13}C\{^{1}H\}$ NMR** (CD_2Cl_2): δ = 37.3 (d, $^{2}J_{CP}$ = 40 Hz, CH_3) ppm.

Synthesis of the Bis(1,2-dihydrazinodiphosphine) (6): A solution of diisopropylamine (0.281 mL, 2 mmol) in CH_2Cl_2 (15 mL) was added dropwise to a solution of compound **5** (124 mg, 0.5 mmol) in CH_2Cl_2 (15 mL), and left to react overnight. The resulting mixture was filtered, and the solution was evaporated to dryness, then washed with cold pentane, to afford compound **6** as a white powder (92 % yield). **$^{31}P\{^{1}H\}$ NMR** (CD_2Cl_2): δ = 112.8 (s) ppm. **^{1}H NMR** (CD_2Cl_2): δ = 0.97 (d, $^{3}J_{HH}$ = 6.8 Hz, 6 H, CH*CH*$_3$), 1.10 (d, $^{3}J_{HH}$ = 6.8 Hz, 6 H, CH*CH*$_3$), 1.17 (d, $^{3}J_{HH}$ = 6.8 Hz, 6 H, CH*CH*$_3$), 1.26 (d, $^{3}J_{HH}$ = 6.8 Hz, 6 H, CH*CH*$_3$), 2.64 (d, $^{3}J_{HP}$ = 7.8 Hz, 6 H, NCH_3), 2.80 (d, $^{3}J_{HP}$ = 12.8 Hz, 6 H, NCH_3), 3.20 (m, 2 H, *CH*CH_3), 4.69 (m, 2 H, *CH*CH_3) ppm. **$^{13}C\{^{1}H\}$ {^{31}P} NMR** (CD_2Cl_2): δ = 20.91 (br. s, *CH*$_3$CH), 22.08 (br. s, *CH*$_3$CH), 26.25 (s, NCH_3), 34.16 (br. s, NCH_3), 43.16 (s, *CH*CH_3), 45.22 (s, *CH*CH_3) ppm. Colorless single crystals suitable for X-ray diffraction were obtained from the solution of **6** in CD_2Cl_2, in the NMR tube.

Synthesis of the bis Ru Complex 7 (*cis* + *trans*): A solution of compound **5** (85 mg, 0.343 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a cooled solution (–80 °C) of $[RuCl_2(p\text{-cymene})]_2$ (210 mg, 0.343 mmol) in CH_2Cl_2 (20 mL), and left to reach slowly room temperature. Evaporation of the solution afforded quantitatively the complex **7** as an orange powder (mixture of two isomers). The signals corresponding to the minor isomer (*trans*) are indicated with *. **$^{31}P\{^{1}H\}$ NMR** (CD_2Cl_2): δ = 165.5 (s, major isomer, ca. 83 %), 164.3* (s, minor isomer, ca. 17 %) ppm. **^{1}H NMR** (CD_2Cl_2): δ = 1.29* (d, $^{3}J_{HH}$ = 6.6 Hz, *CH*$_3$–CH), 1.30 (d, $^{3}J_{HH}$ = 6.8 Hz, 6 H, *CH*$_3$–CH), 1.32 (d, $^{3}J_{HH}$ = 6.9 Hz, 6 H, *CH*$_3$–CH), 2.19 (s, 6 H, CH_3–Cym), 2.20* (s, CH_3–Cym), 2.99 (sept, $^{3}J_{HH}$ = 6.9 Hz, 2 H, CH_3–*CH*), 3.20 (d, $^{3}J_{HP}$ = 12.6 Hz, 6 H, CH_3–N), 3.20* (d, $^{3}J_{HP}$ = 7.8 Hz, CH_3–N), 3.24 (d, $^{3}J_{HP}$ = 9.3 Hz, 6 H, CH_3–N), 5.33–5.75 (m, 8 H, H of cym) ppm. **$^{13}C\{^{1}H\}$ {^{31}P} NMR** (CD_2Cl_2): δ = 17.68 (*CH*$_3$–Cym), 21.42 (*CH*$_3$–CH), 21.69* (*CH*$_3$–CH), 22.15 (*CH*$_3$–CH), 30.60* (CH_3–*CH*), 30.66 (CH_3–*CH*), 38.36 (CH_3–N), 38.54 (CH_3–N), 87.51 (CH of Cym), 88.47 (CH of Cym), 92.72 (CH of Cym), 93.89 (CH of Cym), 99.00* (C of Cym), 100.01 (C of Cym), 111.21* (C of Cym), 111.44 (C of Cym) ppm. **FAB-MS** (MNBA) *m*/*z*: 862 (M^+, calcd. for $[C_{24}H_{40}Cl_6N_4P_2Ru_2]$ 862). $C_{24}H_{40}Cl_6N_4P_2Ru_2$ (861.42): calcd. C 33.46; H 4.68; N 6.50 %; found: C 32.94; H 4.25; N 6.32 %. Orange single crystals suitable for X-ray diffraction were obtained from the solution of **7** in (wet) CD_2Cl_2, in the NMR tube.

Synthesis of the Ru Complex 8: Methanol (2 mL) was added to the solution of the mixture (20 mg) of complexes **7-cis** and **7-trans** in 2 mL of CH_2Cl_2. The reaction mixture was allowed to stay for 7 d, then evaporated to dryness. Purification was carried out by a reprecipitation of the product from its solution in dichloromethane with petroleum ether to afford complex **8** as an orange powder. The NMR spectroscopic data (^{31}P, ^{1}H, ^{13}C) are identical to those reported previously.[25]

Crystal Structure Determinations: Data collection was collected at low temperature with a Xcalibur Oxford Diffraction or IPDS STOE diffractometers using a graphite-monochromated Mo-K_α radiation and equipped with an Oxford Cryosystems Cryostream cooler device. The structures were solved by direct Methods using SIR92,[26] and refined by means of least-squares procedures on *F* using the programs of the PC version of CRYSTALS.[27] The atomic scattering factors were taken from International tables for X-ray Crystallography.[28] All non-hydrogen atoms were refined anisotropically (excepting H_2O mol-

ecules in compound **7**). Compound **3** contains two disordered half molecules per asymmetric unit. Hydrogen atoms were introduced in calculated positions in the last refinements and were allocated an overall refinable isotropic thermal parameter.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1541101 for compound **3**, CCDC-1541103 for compound **6**, and CCDC-1541102 for compound **7** (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): ^{31}P and ^{1}H NMR spectra of compounds **2**, **4**, and **6**.

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