[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 CB2 1EZ, 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**

F. Ekkehardt Hahn,* Lars Wittenbecher, Duc Le Van, Roland Fröhlich, and Birgit Wibbeling

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≡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≡C*t*Bu (**2a**) or P≡C-N*i*Pr$_2$ (**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{^{1}H} 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 ^{1}H 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 σ^3-P–C_{Ring} bond (1.721(2) Å) is noticeably shorter than the other σ^2-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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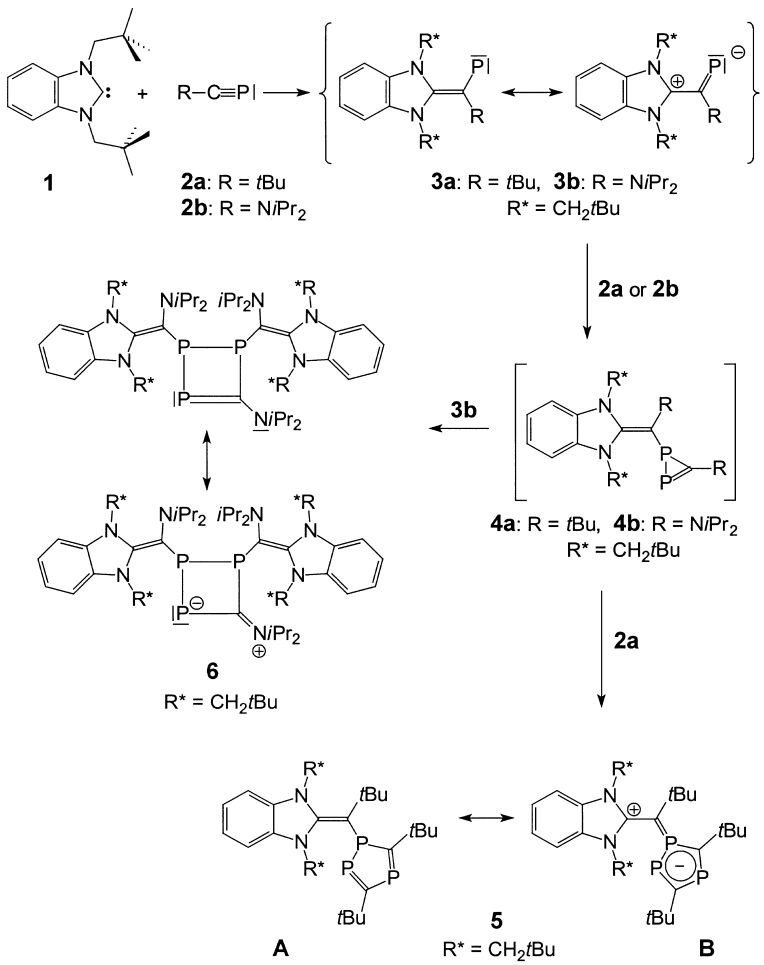

Scheme 1. Proposed mechanism for the formation of **5** and **6**.

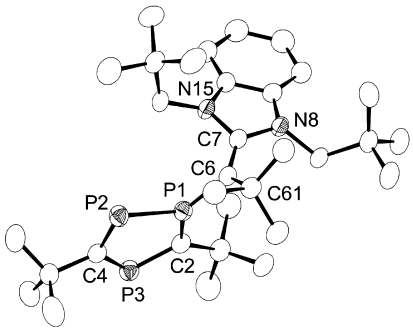

Figure 1. Molecular structure of **5** in the crystal. Selected bond lengths [Å] and angles [°]: P1-P2 2.0853(8), P1-C2 1.721(2), P1-C6 1.757(2), P3-C2 1.736(2), P3-C4 1.739(2), P2-C4 1.734(2), C6-C7 1.406(3), C7-N8 1.394(3), C7-N15 1.380(3); C2-P1-P2 106.33(8), C6-P1-P2 125.31(8), C2-P1-C6 128.15(11), P1-C2-P3 113.83(12), C2-P3-C4 102.97(11), P1-P2-C4 94.90(8), P2-C4-P3 121.92(13), P1-C6-C7 116.1(2), P1-C6-C61 118.0(2), C7-C6-C61 125.9(2), N8-C7-N15 105.5(2), N8-C7-C6 129.2(2), N15-C7-C6 125.1(2).

phole. In contrast to the triphospholes previously described,[5] **5** has mesomerically stabilizing substituents on the tricoordinate phosphorus atom. Both the steric bulk of these ligands,[5b] and the participation of the polar resonance structures **B** in the ground state of the system (Scheme 1), can be considered as possible causes for the leveling out of the ring. The molecular structure of **5** shows a strong twisting (ca. 60°) of the benzimidazol-2-ylidene plane towards the C7-C6-C61-P1 plane, which in turn, is twisted with respect to the plane of the triphosphole ring. An effective conjugation between these sections of the molecule seems to be thus out of the question. Evidently the sterically hindered groups on the C6 atom are also responsible for the lengthening of the C6–C7 double bond to 1.406(3) Å.

Under comparable reaction conditions, the aminophosphaalkyne **2b** behaves differently than **2a** toward **1**. In the reaction of **2b**, the time taken for its complete consumption was only about 15 min (monitored by ^{31}P NMR spectroscopy), during which time the air-sensitive 1,2,3-triphosphetene **6** crystallized out as the only product. The ^{31}P{^{1}H} NMR spectra of **6** show the presence of three stereoisomers (molar ratio 1:1:0.5) in solution. The signal patterns and coupling constants of the isomers are in agreement with the literature data for four-membered rings of this type.[6b, 6c] The strong high-field shift of the signal of the $\lambda^3\sigma^2$-P atom is typical of *C*-aminophosphaalkenes, and demonstrates an effective π-donation from the amino-nitrogen atom. The molecular structure of **6** was unequivocally established by crystal structure analysis[8] (Figure 2). As expected, the four-membered heterocycle is not planar (torsion angle C28-P1-P2-P3 14.2°). The two different bond lengths (P1–P2 2.195(2) Å and P2–P3 2.249(2) Å) are based on the decreased covalent radius of the dicoordinate P atom. The stretching of the P1–C28 bond (1.739(2) Å), the planar environment of the N29 atom (sum of the angles 357.6°), and the shortening of the C28–N29 bond (1.362(2) Å), all suggest a π-delocalization in the N29-C28-P1 fragment. The C–C double bonds on the periphery of the four-membered ring are unusually long in comparison to those in dimerized *N*,*N*′-stabilized carbenes (C1–C2 1.389(3), C41–C42

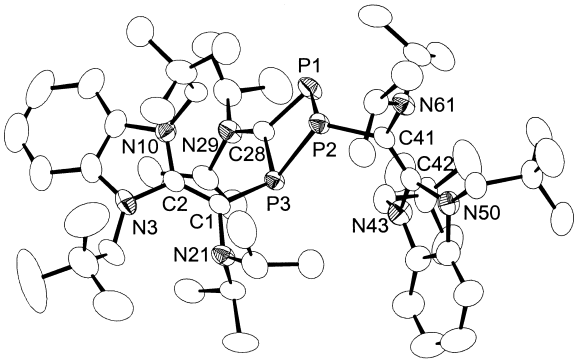

Figure 2. Molecular structure of **6** in the crystal. Selected bond lengths [Å] and angles [°]: P1-P2 2.1952(9), P3-C1 1.832(2), P1-C28 1.739(2), P2-P3 2.2497(9), P2-C41 1.841(2), P3-C28 1.827(2), C28-N29 1.362(2), C1-N21 1.451(2), C1-C2 1.389(3), C2-N3 1.415(2), C2-N10 1.400(3), C41-N61 1.452(2), C41-C42 1.374(3), C42-N43 1.417(2), C42-N50 1.422(2); P1-P2-P3 79.35(3), P1-C28-P3 105.43(10), P2-P1-C28 87.06(7), P2-P3-C28 83.37(6), P1-C28-N29 128.28(14), P3-C28-N29 125.86(14), P3-C1-C2 125.90(14), P3-C1-N21 114.38(14), C2-C1-N21 118.8(2), N3-C2-N10 105.4(2), P2-C41-C42 128.73(14), P2-C41-N61 110.97(14), C42-C41-N61 118.7(2), N43-C42-N50 103.9(2).

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1.374(3) Å) and display large torsional angles (N10-C2-C1-P3 −18.7°, N3-C2-C1-N21 −18.2°, N43-C42-C41-P2 22.8°, N50-C42-C41-N61 19.2°). In order to minimize the steric interactions, the two neopentyl groups on the ring nitrogen atom in **6**, as in **5**, and the complex [W(CO)$_5$ (**1**)],[7] are positioned on the same side of the N-heterocycle.

Whilst no intermediates were detected by ^{31}P NMR monitoring of the reaction of the carbene **1** with **2a**, the analogous reaction with **2b** yielded two mutually coupled doublets of the same intensity, which disappeared over the period of a few hours in favor of the phosphorus signal of **6**. The high-field position of these temporary ^{31}P NMR signals (−183.3 and −66.3) and their ^1J(P,P) coupling constants (97.7 Hz) are comparable to the data for the amino-substituted 1*H*-diphosphirenes,[9] and give rise to the suggestion that the nonisolable 1*H*-diphosphirene **4b** is present. On the basis of this assumption, we postulate a multistep process for the selective production of **5** and **6** (Scheme 1). The reaction commences with the addition of the nucleophilic carbene **1** to **2a** or **2b** to form the highly reactive species **3a** or **3b**, respectively. However, the possibility that the 2*H*-phosphirenes are formed first, as with the addition of the halocarbenes to phosphaalkynes,[1] cannot be ruled out. The ensuing [2+1] cycloaddition of **3a** or **3b** to a further molecule of the phosphaalkyne delivers the 1*H*-diphosphirene **4a** or **4b**, respectively. Compound **4a** is capable, after ring opening, of undergoing a [3+2] cycloaddition with the *tert*-butylphosphaacetylene **2a** to form **5**. In the case of **4b**, the insertion previously described in the literature of phosphinidenes into the P–P diphosphirene bond[6a] (here **3b** into **4b**) leads to the four-membered heterocycle **6**. The reaction sequence (**4a** →**5**) has already been discussed in the literature.[10] The cause of the difference in the end products obtained from the reaction of **1** with **2a** or **2b** lies clearly in the difference in the polarity between the two related phosphaalkynes. Compound **2b** is known to have a higher reactivity toward polar reagents than **2a**, due to the donor substituents.[6b, 11]

Compounds **5** and **6** presented herein are not only the first 1,2,4-triphosphole and 1,2,3-triphosphetene derivatives to carry reactive olefinic bonds on their substituents, but they contain a long unknown structural element, namely the combination of two heteroatom-substituted carbenes N(N)C: and P(C)C: or P(N)C:, respectively. In view of the recently demonstrated cleavage of entetramines,[12] compounds of type **6** could in particular find use in the preparation of new N,N,N,P-substituted olefins and of stable N,P-substituted carbenes.

Experimental Section

All reactions were carried out under argon using standard Schlenk techniques. Solvents were dried and then distilled and stored under argon. Reactions were monitored by using ^{31}P NMR spectroscopy.

5: A solution of **2a**[13a] (0.10 g, 1.0 mmol) in C_6D_6 (0.5 mL) was added at room temperature to a solution of **1**[7] (0.26 g, 1.0 mmol) in C_6D_6 (1 mL). The dark red solution was stirred for 48 h at 25 °C, during which time red crystals of **5** were formed in the solution. After filtration and drying at 0.5 Torr, **5** was obtained in 92% yield (0.17 g). Unconverted carbene **1** remained in solution during this procedure. ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6, 25 °C, numbering: see Figure 1): δ = 224.8 (P3), 178.5 (P2), 111.3 (P1), ^1J(P1,P2) = 528.1, ^2J(P1,P3) = 17.2, ^2J(P2,P3) = 40.5 Hz; ^{1}H NMR (200.1 MHz, C_6D_6, 25 °C): δ = 0.86 (s, 9H; $CH_2CC\mathit{H_3}$), 0.96 (s, 9H; $CH_2CC\mathit{H_3}$), 1.44 (d, ^3J(P,H) = 1.4 Hz, 9H; PCCC$\mathit{H_3}$), 1.60(s, 9H; PCCC$\mathit{H_3}$), 1.85 (d, ^3J(P,H) = 0.8 Hz, 9H; PCCC$\mathit{H_3}$), 4.55 (s, 4H; NCH_2), 6.50 (m, 4H, Ar-H); ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6, 25 °C): δ = 201.7 (ddd, ^1J(P,C) = 73.4, ^1J(P,C) = 64.8, ^2J(P,C) = 20.5 Hz; PC(4)P), 180.5 (ddd, ^1J(P,C) = 70.4, ^1J(P,C) = 17.6, ^2J(P,C) = 9.7 Hz; PC(2)P), 159.8 (d, ^2J(P,C) = 4.5 Hz; NCN), 67.2 (ddd, ^1J(P,C) = 36.2, ^2J(P,C) = 5.2, ^3J(P,C) = 2.3 Hz, C*C*tBu), 143.6, 135.6, 121.7, 118.9, 110.9, 105.4 (Ar-C), 64.2 (s; CH_2), 57.0 (s; CH_2), 41.7 (ddd, ^2J(P,C) = 40.9, ^2J(P,C) = 18.3, ^3J(P,C) = 8.6 Hz; *C*Me$_3$), 40.0 (dd, ^2J(P,C) = 20.8, ^2J(P,C) = 3.0 Hz; *C*Me$_3$), 36.3 (dd, ^2J(P,C) = 11.4, ^3J(P,C) = 2.5 Hz; *C*Me$_3$), 36.0 (s; CH_2CMe$_3$), 35.8 (s; CH_2CMe$_3$), 34.0 (d, ^3J(P,C) = 4.2 Hz; CH_3), 33.9 (d, ^3J(P,C) = 2.7 Hz; CH_3), 33.8 (d, ^3J(P,C) = 3.2 Hz; CH_3), 30.0 (s; $CH_2CC\mathit{H_3}$), 27.9 (s; $CH_2CC\mathit{H_3}$); MS (70 eV): *m*/*z* (%): 558 (100) [M^+], 543 (54) [$M^+ - CH_3$], 501 (8) [$M^+ - t$Bu], 327 (11) [$M^+ - P_3C_2t$Bu$_2$].

6: As described for **5**, 0.08 g (90%) yellow crystals, suitable for X-ray analysis, were obtained from **1** (0.07 g, 0.28 mmol) and **2b** (0.04 g, 0.28 mmol).[13b] ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6, 25 °C; mixture of isomers, molar ratio: a:b:c = 1:1:0.5; numbering: see Figure 2), isomer a: δ = 86.5 (P1), −58.5 (P2), 9.5 (P3), ^1J(P1,P2) = 255.8, ^2J(P1,P3) = 55.8, ^2J(P2,P3) = 249.8 Hz; isomer b: δ = 96.3 (P1), −45.0 (P2), 19.8 (P3), ^1J(P1,P2) = 246.8, ^2J(P1,P3) = 62.7, ^2J(P2,P3) = 238.0 Hz; isomer c: δ = 121.1 (P1), −62.1 (P2), 18.0 (P3), ^1J(P1,P2) = 242.0, ^2J(P1,P3) = 64.1, ^2J(P2,P3) = 230.0 Hz; ^{1}H NMR (mixture of isomers, 200.1 MHz, C_6D_6, 25 °C): δ = 0.59–1.29 (72H, CH_3), 2.8–4.2 (br., 14H, CH_2, CH), 6.5–6.8 (m, 8H, Ar-H).

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[8] a) X-ray structure analysis of **5** ($C_{32}H_{53}N_2P_3$): M_r = 558.67, red crystals 0.30 × 0.30 × 0.10 mm, a = 9.450(1), b = 24.111(1), c = 14.570(1) Å, β = 97.97(1)°, V = 3287.7(4) Å^3, ρ_{calcd} = 1.129 g cm^{-3}, μ = 2.03 cm^{-1}, empirical absorption correction with SORTAV (0.942 ≤ T ≤ 0.980), Z = 4, monoclinic, space group $P2_1/c$ (no. 14), λ = 0.71073 Å, T = 198 K, ω and φ scans, 13894 measured reflections ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.65 Å^{-1}, 7512 independent (R_{int} = 0.060) and 5241 observed reflec-

tions [$I \geq 2\sigma(I)$], 349 refined parameters, $R = 0.055$, $wR^2 = 0.133$, max/min residual electron density 0.35/ − 0.34 e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.[14] b) X-ray structure analysis of **6** ($C_{55}H_{94}N_7P_3$): $M_r = 946.28$, yellow crystals 0.25 × 0.20 × 0.10 mm, $a = 10.995(2)$, $b = 15.658(3)$, $c = 17.031(3)$ Å, $\alpha = 80.33(3)$, $\beta = 88.60(3)$, $\gamma = 82.72(3)^\circ$, $V = 2867.1(9)$ Å^3, $\rho_{calcd} = 1.096$ g cm^{-3}, $\mu = 12.46$ cm^{-1}, empirical absorption correction by using ψ scan data ($0.746 \geq T \geq 0.886$), $Z = 2$, triclinic, space group $P\bar{1}$ (no. 2), $\lambda = 1.54178$ Å, $T = 223$ K, $\omega/2\theta$ scans, 12328 measured reflections ($+h$, $\pm k$, $\pm l$), [$(\sin\theta)/\lambda$] = 0.62 Å^{-1}, 11688 independent ($R_{int} = 0.016$) and 9440 observed reflections [$I \geq 2\sigma(I)$], 660 refined parameters, $R = 0.053$, $wR^2 = 0.167$, max/min residual electron density 0.43/ − 0.167 e Å^{-3}, disorder of the *tert*-butyl groups at C12 and C17 are described with split positions and geometric constraints, hydrogen atoms calculated and refined as riding atoms.[14]

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[14] All data sets were collected on a Enraf Nonius CAD4 or a Nonius Kappa-CCD diffractometer with a rotating anode FR591 (Nonius) used as a radiation source. The following programs were used: EXPRESS (Nonius B. V., 1994) and COLLECT (Nonius B. V., 1998) for data collection; MolEN (K. Fair, Enraf-Nonius B. V., 1990) and Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307 – 326) for data reduction; SORTAV for absorption correction of CCD-Data (R. H. Blessing, *Acta Crystallogr. Sect. A* **1995**, *51*, 33 – 37; R. H. Blessing, *J. Appl. Crystallogr.* **1997**, *30*, 421 – 426); SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467 – 473) for structure solution; SHELXL-97 (G. M. Sheldrick, Universität Göttingen, **1997**) for structure refinement. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-139113 (**5**) and CCDC-139114 (**6**). 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).

Designing a Heterogeneous Catalyst for the Production of Adipic Acid by Aerial Oxidation of Cyclohexane**

Markus Dugal, Gopinathan Sankar, Robert Raja, and John Meurig Thomas*

Dedicated to Professor Helmut Knözinger on the occasion of his 65th birthday

Adipic acid (AA) is an important building block for a variety of commercially useful products such as polyamides (nylon 6.6) and urethanes.[1] Currently, it is manufactured mainly by a two-step process involving nitric acid oxidation of cylohexanone and cyclohexanol. The latter compound is generated from cyclohexane using homogeneous (cobalt-based) catalysts, often in combination with promoters and peroxides.[2–4] Alternative synthetic routes have been developed, such as the one-step oxidation of cyclohexane with either alkyl hydroperoxide as oxidant and a catalyst consisting of cobalt salts[5, 6] or dioxygen as oxidant and a cobalt acetate catalyst in acetic acid.[7] More recent industrial syntheses include the homogeneously catalysed hydrocarboxylation[8, 9] or carboalkoxylation[10] of butadiene. For the research chemist, the intellectual challenge is to devise a strategy for a one-step production of AA from hydrocarbons using an appropriately designed, heterogeneous catalyst that functions with air or dioxygen as the oxidant. Such a catalyst would allow facile separation and recycling while simultaneously avoiding the use of hazardous or corrosive reagents. Herein, we report progress towards this goal. The iron-based, framework-substituted, molecular-sieve catalyst that we describe exhibits good performance in the direct low-temperature conversion of cyclohexane to AA in air.

Based on our recent work on the selective aerial oxidation of alkanes at the terminal position[11] and, in particular, the selective aerial conversion of cyclohexane to cyclohexanol and cyclohexanone using transition metal ion substituted, microporous aluminium phosphates (MAPOs),[12, 13] we argued that it was necessary to assemble an Fe^{III}-substituted MAPO structure in which the pore aperture is significantly smaller than that of FeAlPO-5 (7.3 Å diameter). This structure creates a constrained environment for the cyclohexane oxidation (see Figure 1) and thus modifies the selectivity of the reaction. What we capitalize upon is shape-selective catalysis[14, 15] using a carefully designed microporous solid. In our previous work, we showed[16] for hydrocarbons small enough to enter into a microporous catalyst, the free radical oxidation of these materials proceeds in a highly localized manner in the restricted environment of the catalytically active sites at which the M^{III} ions are exposed on the

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