$[Pt_{19}(CO)_{21}(NO)]^{3-}$ and $[Pt_{38}(CO)_{44}]^{2-}$: Nitrosyl Bending through Intramolecular Electron Transfer as an Intermediate Step in the Nucleation Process from Polydecker to *ccp* Platinum Carbonyl Clusters[**]

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In memory of Paolo Chini

High-nuclearity carbonyl metal clusters (HNCCs) are often considered to be excellent model systems for studying important events concerning small metal particles, for example chemisorption and catalytic activity, which are highly dependent on the local structure of the active sites (exposed faces, surface defects, kinks, steps).[1] Several different metal packings have been found in HNCCs, but still little information is available about skeletal transformations, nucleation processes, and ligand activation.[2, 3] Several years ago we reported the synthesis and the crystal structure determination of $[Pt_{19}(CO)_{22}]^{4-}$ (**1**), which contains a principal axis of idealized fivefold symmetry.[4] At that time $[Pt_{38}(CO)_{44}]^{2-}$ (**2**) was also isolated from the reaction of **1** with protic acids; however, the poor quality of the miscellaneous crystals of **2** obtained over the years defeated all attempts to fully elucidate its structure and only disclosed a *ccp* Pt_{38} cluster core.[5] Consequently, the number of cations and carbonyl ligands could only be inferred from elemental analyses[5] and theoretical expectations.[6]

The exceptional redox propensity of **1** and **2** pointed out by electrochemical and spectroelectrochemical studies[5b, 7] prompted us to reinvestigate the chemistry of **1** with the aim to explore the effect of its electron-sponge behavior toward coordinated ligands other than CO. A further objective was to gain better understanding of the nucleation process leading from the fivefold symmetry core of **1** to the *ccp* core of **2**. We report here the synthesis and molecular structure of the unprecedented nitrosyl HNCC $[Pt_{19}(CO)_{21}(NO)]^{3-}$ (**3**). As a part of these studies, a new synthesis and the full structural characterization of **2**, which disclosed the exact stereochemistry of all carbonyl ligands, is also reported.

Compound **3** has been obtained by controlled addition of one equivalent of $NOBF_4$ to a solution of **1** in acetonitrile at room temperature and under nitrogen atmosphere [Eq. (1)]. Apparently, Equation (1) represents the plain sub-

$$\underset{\mathbf{1}}{[Pt_{19}(CO)_{22}]^{4-}} + NO^{+} \longrightarrow \underset{\mathbf{3}}{[Pt_{19}(CO)_{21}(NO)]^{3-}} + CO \tag{1}$$

stitution of a carbonyl with a nitrosyl ligand. However, as we will show, **1** and **3** cannot be considered isoelectronic, and the latter has two cluster valence electrons (CVEs) less than the former. The IR spectrum of **3** in acetonitrile shows absorption bands assigned to terminal (2025s, 1965w cm^{-1}) and edge-bridging carbonyl groups (1817 cm^{-1}) and bent nitrosyl ligands (1617w cm^{-1}); the latter absorption is clearly observed also when crystals of $[PPh_4]_3$-**3** are dissolved in THF.

Further gradual addition of two equivalents of $NOBF_4$ to **3** in acetonitrile leads to different products as a function of the reaction atmosphere. Thus, under a carbon monoxide atmosphere, the reaction of **3** with NO^+ selectively leads to **2**, which separates out as a sparingly soluble quaternary ammonium or phosphonium salt [Eq. (2)].

$$2\underset{\mathbf{3}}{[Pt_{19}(CO)_{21}(NO)]^{3-}} + 4NO^{+} + 2CO \longrightarrow \underset{\mathbf{2}}{[Pt_{38}(CO)_{44}]^{2-}} + 6NO \tag{2}$$

According to the sum of Equations (1) and (2), the direct transformation of **1** into **2** can be conveniently carried out by adding three equivalents of $NOBF_4$ to **1** under a carbon monoxide atmosphere. Compound **2** shows two sharp IR absorptions (2056s, 1807m cm^{-1}) in THF. In contrast, under a nitrogen atmosphere, monitoring by IR spectroscopy suggests the additional formation of yet uncharacterized oxidized species not containing metal-bound nitrosyl groups.

The molecular structure of **3** has been determined by X-ray diffraction on a single crystal of its PPh_4^+ salt. The asymmetric unit contains two crystallographically independent (but very similar) anions.[8] As in the parent species **1**, each anion contains a Pt_{19} metal core derived from the fusion of three pentagonal bipyramids along a common axis, resulting in a Pt-Pt_5-Pt-Pt_5-Pt-Pt_5-Pt array of idealized D_{5h} symmetry (Figure 1). Eleven terminal and ten edge-bridging carbonyl groups and one terminally bonded nitrosyl group surround the metal core and, if the differences in the C/N labels are neglected, the connectivity pattern of **1** is fully maintained. Since the metal core and ligand geometries of the two independent moieties of **3** are strictly comparable and match (to within 0.03 Å) the average values for the eight chemically distinct sets of intermetallic distances of the parent species **1** (see legend to Figure 1), the original detailed discussion on the nature of the different metal–metal interactions in **1** holds also for **3**.

The coordination of the NO fragment, which occurs selectively on one apical Pt atom, can be easily evinced by the bent Pt-N-O angles (142(2) and 150(2)°); all other terminal ligands show M-C-O values in the 172(2)–179(2)° range.[9] Bent σ-bonded nitrosyl ligands typically show M-N-O angles between 120 and 160°.[10] Such observed bending points

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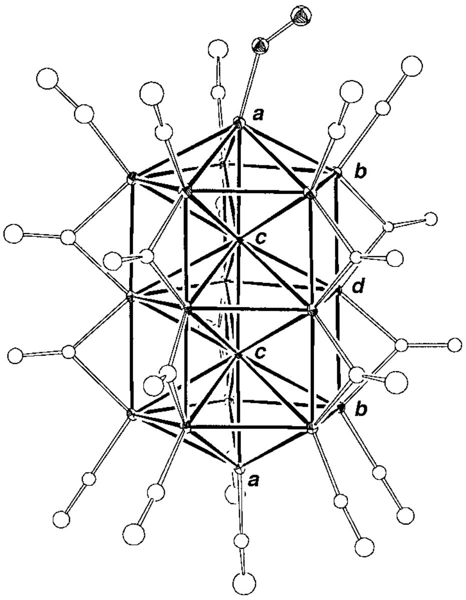

Figure 1. ORTEP drawing of **3** showing the unique nitrosyl ligand on one apical Pt atom. Thermal ellipsoids are drawn at the 50 % probability level. Average Pt ··· Pt distances [Å] (values for **1** in parentheses): *a–b* (20 ×) 2.74 (2.75), *a–c* (4 ×) 2.66 (2.68), *b–c* (20 ×) 2.79 (2.81), *b–d* (20 ×) 2.72 (2.72), *c–d* (20 ×) 2.79 (2.80), *c–c* (2 ×) 2.64 (2.64), *b–b* (20 ×) 2.86 (2.87), *d–d* (10 ×) 2.87 (2.90); additional bond distances [Å] and angles [°]: Pt–N 1.79(2) – 1.82(2), N–O 1.14(2) – 1.15(2), av $C{-}O_{terminal}$ 1.16, av $C{-}O_{bridging}$ 1.21; Pt-N-O 142(1) – 150(2).

out that the nitrosyl group of **3** is σ-bonded and formally behaves as a one-electron donor. Evidently, a redistribution of CVEs (from 238 in **1** to 236 in **3**) has occurred by means of an intramolecular redox reaction, which localizes onto the NO ligand two electrons formerly delocalized over the metal cluster. Therefore, it appears that the versatile NO fragment, in its linear or bent mode, could stabilize isostructural clusters with different numbers of CVEs, like those observed in the electrochemical oxidation of **1**.[7]

The intramolecular redox reaction leading to **3** has been rationalized by semiempirical extended Hückel (EH) molecular orbital computations with CACAO[11] on a $[Pt_{19}(CO)_{21}]^{3-}$ fragment of idealized C_{5v} symmetry interacting with a terminally bonded NO ligand. These point out that the stabilization deriving from the $\pi^*(NO) - d_{xz}, d_{z^2}$ interaction in the bent mode overwhelms the destabilizing $\sigma(NO) - d_{z^2}$ overlap.[12] Furthermore, a Walsh diagram reveals a minimum of the EH total orbital energy for Pt-N-O bending close to 140°, which is in agreement with the experimental value. That this rationalization is at least qualitatively reliable has been shown by computing also the corresponding diagrams of the mononuclear species $[M(S_2CNR_2)_2(NO)]$ (M = Fe, R = Et[13] and M = Co, R = Me[14]) bearing a linear and bent nitrosyl ligand, respectively, and the most relevant $[Pt_{19}(CO)_{21}(CO)]^{4-}$ anion (**1**, for which the linear geometry of the apical carbonyl is correctly predicted).

Coordination of bent NO on electron-rich metal centers is well documented; bending of linear metal-bound NO has been suggested to occur upon reduction or photochemical excitation on the basis of spectroscopic studies and is thought to prelude NO activation in a number of reactions.[15] To our knowledge **3** is the first structurally characterized carbonyl cluster bearing a bent nitrosyl group.

The structure of **2**, as derived from its $[N(PPh_3)_2]^+$ salt,[8] is based on the previously ascertained *ccp* metal core of idealized O_h symmetry (Figure 2). The 38 platinum atoms constitute a truncated ν_3 octahedron with only three chemically distinct types of metal atoms: 6 in *a*, 8 in *b*, and 24 in *d* (Wyckoff positions of the O_h point group). In addition, this cluster bears 32 terminal carbonyl groups (one on each surface atom (*b* and *d*)) and 12 edge-bridging CO ligands (two on opposite sides of the six square faces made by *d* atoms); the overall idealized symmetry is thus lowered to D_{2d} (Figure 3).

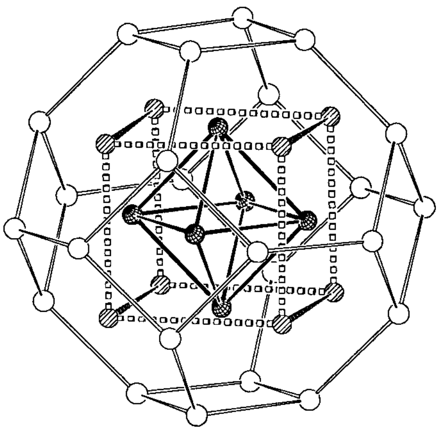

Figure 2. Perspective drawing of the Pt_{38} metal cage of **2** showing the Pt_6 octahedron encapsulated in a shell of 32 Pt atoms with O_h symmetry. Empty circle: Wyckoff *d* position, hatched circle: Wyckoff *b* position, cross-hatched circle: Wyckoff *a* position. Average Pt ··· Pt distances [Å]: *a–a* (12 ×) 2.881(5), *a–b* (24 ×) 2.784(28), *a–d* (24 ×) 2.859(37), *b–d* (48 ×) 2.848(31), *d–d* (24 ×) 2.844(23). Mean values and estimated standard deviations (in parentheses) of chemically equivalent interactions computed as $x_{av} = 1/n\Sigma x_i$ and $\sigma^2_{n-1} = 1/(n-1)\Sigma(x_i - x_{av})^2$.

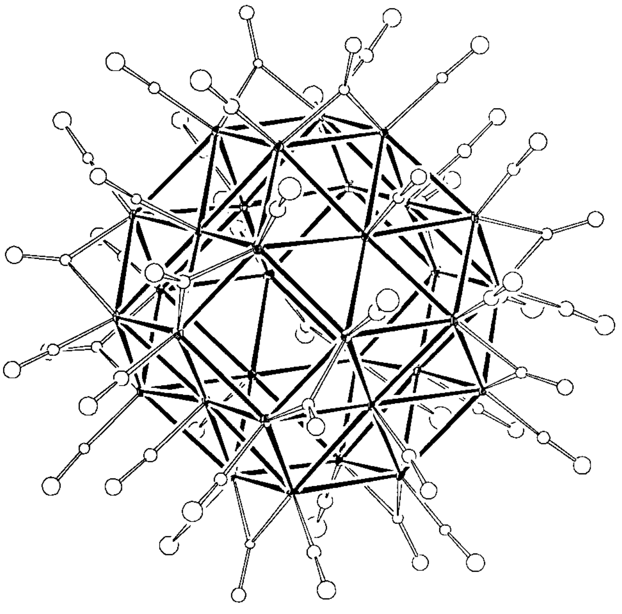

Figure 3. ORTEP drawing of **2**. For simplicity the inner Pt_6 octahedron has been removed. Thermal ellipsoids are drawn at the 50 % probability level; av $C{-}O_{terminal}$ 1.15, av $C{-}O_{bridging}$ 1.22 Å.

While the Pt$\cdots$Pt distances lie in the 2.749(1)–2.919(1) Å range, a much more uniform distribution is observed for the fully encapsulated Pt_6 octahedron (2.803(1)–2.818(1) Å), which does not suffer from the less symmetric environment sustained by the surface platinum atoms. These can be divided in two distinct sets: 1) the six centers of slightly concave (average displacement ca. 0.07 Å) hexagons, and 2) the 24 peripheral *d* atoms, showing shorter Pt$\cdots$Pt distances (av 2.814 Å) for carbonyl-bridged edges than for unsupported ones (av 2.859 Å). The analysis of the bond lengths and carbonyl geometry, as well as the adopted synthesis, does not support the presence of hydrides within the cluster or close to its surface.

Yet a limited number of close-packed HNCC containing fully encapsulated groups of metal atoms are known, for example $[Pt_{26}(CO)_{32}]^{2-}$,[5a,b] $[H_{6-n}Ni_{38}Pt_6(CO)_{48}]^{n-}$ ($n = 4$–6),[16] $[Ni_{36+x}Pt_4(CO)_{45+x}]^{6-}$ ($x = 0$, 1),[17] $[H_xRh_{28}N_4(CO)_{41}]^{4-}$ ($x = 0$ or 2),[18] and $[H_{12}Pd_{28}Pt_{13}(CO)_{27}(PMe_3)(PPh_3)_{12}]$.[19] Due to interest in them also as electron-sink compounds,[16b] it is hoped that the recent availability of CCD area detectors could rapidly increase this number. Within this class, compound **2** features the largest homometallic core exclusively stabilized by carbonyl ligands and the smallest polyhedron for which an inner octahedron is fully surrounded by a second shell of metal atoms. In this respect, it is comparable to the well-known species $[H_xRh_{13}(CO)_{24}]^{(5-x)-}$ ($x = 1$–3)[20] and **1**, which encapsulate one and two metal atoms, respectively.[21]

Efforts to clarify the condensation process from **1** to **2**, the reactivity of the bent NO ligand and the redox behavior of **3** are underway.

Experimental Section

$[PPh_4]_3$-**3**: A solution of $NOBF_4$ (10 mg, 0.086 mmol) in acetonitrile (5 mL) was added in small portions to a solution of $[NBu_4]_4$-**1** (460 mg, 0.087 mmol) in acetonitrile (15 mL). The resulting mixture was stirred for about 1 h while the reaction was monitored by IR spectroscopy. The solid product was precipitated and recovered by addition of a solution of PPh_4Cl (500 mg) in isopropanol (40 mL). The resulting solid was filtered, washed with isopropanol (20 mL), and crystallized from acetonitrile (20 mL) and diisopropyl ether (50 mL) to yield 230 mg of $[PPh_4]_3$-**3** (48 % yield based on Pt). Elemental analysis: calcd: C 20.90, H 1.13, N 0.26; found: C 21.00, H 1.05, N 0.20.

$[N(PPh_3)_2]_2$-**2**: $[N(PPh_3)_2]_4$-**1** (1.94 g, 0.3 mmol) was dissolved in acetonitrile (40 mL) under a CO atmosphere. A solution of $NOBF_4$ (105 mg, 0.9 mmol) in acetonitrile (5 mL) was slowly added, and the mixture was stirred for 4 h. The resulting black precipitate was filtered, washed with acetonitrile (10 mL), and crystallized from THF (20 mL) and cyclohexane (60 mL) to yield 580 mg of $[N(PPh_3)_2]_2$-**2** (40 % yield based on Pt). Elemental analysis: calcd: C 14.32, H 0.62, N 0.29; found: C 14.10, H 0.75, N 0.25.

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[8] a) Crystal data for $[PPh_4]_3[Pt_{19}(CO)_{21}(NO)]$ ($[PPh_4]_3$-**3**): triclinic, space group $P\bar{1}$, $a = 19.928(3)$, $b = 23.685(4)$, $c = 24.058(4)$ Å, $\alpha = 113.63(1)$, $\beta = 90.21(1)$, $\gamma = 102.78(1)^\circ$, $V = 10.091(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 3.517\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 263.3\ cm^{-1}$;[8c] b) Crystal data for $[N(PPh_3)_2]_2[Pt_{38}(CO)_{44}]$ ($[N(PPh_3)_2]_2$-**2**): monoclinic, space group $C2/c$, $a = 32.768(2)$, $b = 14.110(2)$, $c = 36.459(2)$ Å, $\beta = 105.80(1)^\circ$, $V = 16{,}220(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 3.98\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 327.2\ cm^{-1}$.[8c] c) Graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Experimental procedure (values for $[N(PPh_3)_2]_2$-**2** in parentheses): 140702 (37301) reflections with $\theta < 30.5$ (26.0)° were measured at 193 K (173 K) on a Bruker SMART diffractometer equipped with a CCD area detector, on a crystal of approximate dimensions 0.10 × 0.15 × 0.25 mm (0.05 × 0.10 × 0.15 mm), mounted in air but protected by a cooling N_2 stream during the data collection. Data were corrected for Lorentz, polarization, and absorption effects (empirical absorption corrections by SADABS: G. M. Sheldrick, unpublished). The structures were solved by direct methods (A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115), and refined with full-matrix least squares (G. M. Sheldrick, *SHELXL97, Program for Structure Refinement*, Universität Göttingen, Germany, **1997**) using 53926 (14000) independent reflections. Anisotropic displacement parameters were assigned to Pt and P atoms. The final agreement factors were $R = 0.050$ (0.056) and $R_w = 0.086$ (0.163); maximum $\Delta\rho = 3.0$ (4.3) $e^-\,Å^{-3}$, close to the Pt atoms. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-127446 (**3**) and CCDC-127447 (**2**). 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).

[9] That such Pt-N-O values are not experimental artifacts stems from the strict similarity of the geometrical parameters derived in the two crystallographically independent anions. In addition, a partial disorder of the NO fragment on the opposite apical platinum atoms is also detectable by slight bending of their unique terminal carbonyls: 161(2)–163(2)°; therefore, the Pt-N-O angles cited in the text are necessarily overestimated.

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The Electrophilic Behavior of Stable Phosphanylcarbenes Towards Phosphorus Lone Pairs[**]

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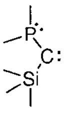
All the known stable carbenes **I**–**VIII**[1, 2] feature two heteroatom substituents. According to calculations,[3] all these carbenes are strongly stabilized by electron donation from the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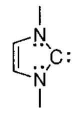
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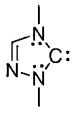
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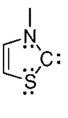
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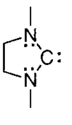
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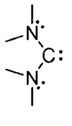
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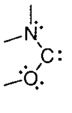
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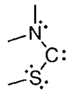
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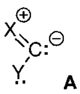
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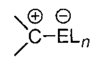
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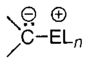
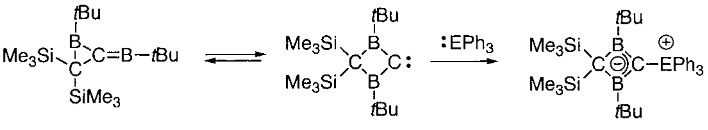

C

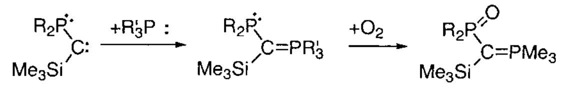
nitrogen or phosphorus lone pair into the formally "empty" p_π orbital. In other words, the peculiar stability of these compounds is due to the crucial contribution of the ylide form **A**. Therefore, carbenes **I**–**VIII** show strong nucleophilic character and readily react with Lewis acids to give reverse ylides **B**.[1, 4] On the other hand, transient electrophilic carbenes are known to react with Lewis bases to give normal ylides **C**. For example, carbene–pyridine adducts have been spectroscopically characterized and used as a proof for the formation of carbenes.[5] The reaction of transient dihalocarbenes with phosphanes is even a preparative method for *C*-dihalo phosphorus ylides.[6] Lastly, addition of triphenylphosphane and triphenylarsane to the borandiylborirane **IX**, the hidden form of the electrophilic carbene **X**, led to the corresponding ylides **XI**.[7] These reactions which involve the vacant orbital of singlet carbenes have not yet been observed with the stable carbenes **I**–**VIII**.



IX **X** **XI**: E = P, As

Moss et al. have shown that in contrast to dialkoxycarbenes, carbenes featuring only a weak π-donor substituent, such as acetoxyphenylcarbene, give carbene–Lewis base adducts.[8] Among the stable carbenes **I**–**VIII**, only the phosphanylsilylcarbene **I** has a single π-donor substituent. Moreover, it has been theoretically[9] and experimentally[10] demonstrated that phosphorus is a weaker π donor than nitrogen. Here we report that the stable carbene **1** indeed reacts with phosphanes to give the corresponding phosphorus ylides; the extension of this reaction to a bimetallic complex containing a side-on-coordinated :P≡P: moiety is also presented.

Instantaneous and quantitative formation of phosphorus ylides **2** occurred when one equivalent of phosphane was added at 0 °C to a solution of carbene **1** in pentane (Scheme 1).[11] The coupling of the phosphane with the carbene center was indicated by AX systems in the ^{31}P NMR spectra. Ylides **2** are highly sensitive to oxygen. Attempted recrystallizations of **2a** led to the corresponding phosphane oxide **3a**, which was isolated in 90 % yield, as colorless crystals suitable for an X-ray diffraction study (Figure 1).[12] The formation of **2** clearly demonstrates that the derivative **1** possesses an available vacant orbital at the carbene center, as



1 **2** **3a**

Scheme 1. Synthesis of *C*-phosphanyl phosphorus ylides **2** and oxidation of **2a** to **3a**. R = cHex$_2$N; $R'_3 = Me_3P$ (**a**), Et_3P (**b**), Me_2PhP (**c**), $MePh_2P$ (**d**), Ph_3P (**e**).

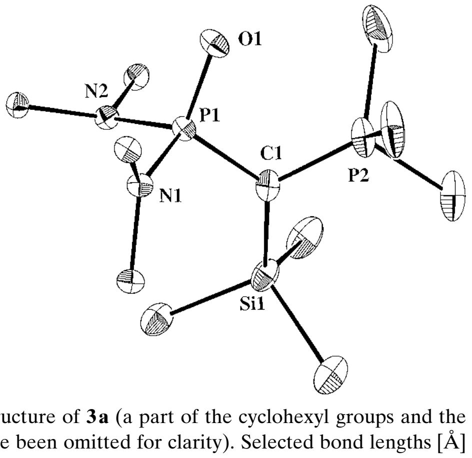


Figure 1. Crystal structure of **3a** (a part of the cyclohexyl groups and the hydrogen atoms have been omitted for clarity). Selected bond lengths [Å] and angles [°]: P1–C1 1.755(2), P1–O1 1.4867(16), P2–C1 1.707(2), C1–Si1 1.849(2); P1-C1-P2 110.58(13), P1-C1-Si1 130.04(13), P2-C1-Si1 118.69(12).

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