

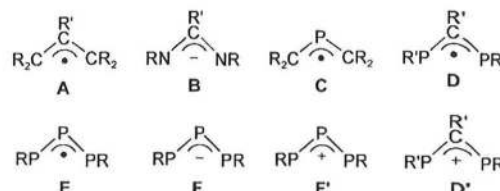
The Complexed Triphosphaallyl Radical, Cation, and Anion Family**

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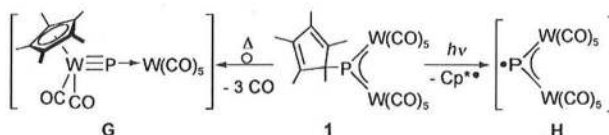
Dedicated to Professor Joachim Sauer on the occasion of his 60th birthday

The allyl radical **A** is of fundamental importance in both experimental and theoretical organic chemistry.^[1-4] Structures of allyl radical compounds stabilized by bulky substituents have been reported by the research groups of Streitwieser^[3] and Azuma.^[4] Moreover, the allyl anion and the amidinato ligand **B**, the latter formed by the replacement of CR₂ by isolobal NR moieties, are prominent ligands in coordination chemistry. Amidinate ligands **B**, which have bulky substituents on the N atoms, have been used to stabilize molecules in unusual bonding situations.^[5-10] The replacement of CR' in the allyl radical **A** by isolobal phosphorus gives a 2-phosphaallyl radical **C**. Compounds of type **C** have only been synthesized in situ by electrochemical reduction of 2-phosphaallyl cations,^[11] and their structural parameters have been calculated by using quantum chemical methods.^[12] The stability of such systems can be increased by embedding the radical in a four-membered 1,3-diphosphacyclobutenyl ring system.^[13,14] The replacement of the terminal CR₂ groups by isolobal PR' fragments in **A** to yield the 1,3-diphosphaallyl radical **D**,^[15] as well as its cationic derivative **D'** (R' = NR₂),^[16] were reported by Bertrand and co-workers. However, no crystallographic proof for the structures of these compounds has been reported to date. Complete isolobal replacement of the CR units in the allyl radical **A** by P leads to the triphosphaallyl radical **E**, which is also unreported to date. Herein, we report a straightforward synthesis of an air-stable complexed triphosphaallyl radical **E** by photolysis of the Cp* containing (Cp* = C₅Me₅) phosphinidene complex with a diphosphene and its transformation into its anionic (**F**) and cationic (**F'**) derivatives.^[17] Interestingly, Jutzi et al. have reported spec-

troscopic evidence for the anion **F** and its 2-arsa congener.^[18]



We have shown that the phosphinidene complex [Cp*P(W(CO)₅)₂] (**1**)^[19] is an excellent starting material for the in situ generation of intermediate **G**,^[20] which contains a tungsten-phosphorus triple bond (Scheme 1). The intermedi-



Scheme 1. Different transformation pathways in the photolysis and thermolysis of **1**.

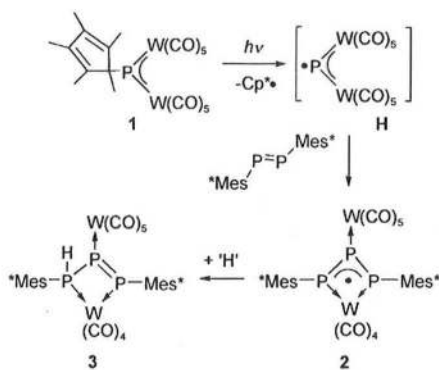
ate can be trapped by organometallic compounds that contain multiple metal-metal bonds,^[21] alkynes,^[22] and phosphalkynes to give novel clusters, metal-containing heterocycles, or cage compounds. In the latter reaction, an unusual opening of the Cp* ligand is observed to form an unprecedented 1,2-diphosphacyclooctatetraene ligand.^[23] Compound **G** is formed by Cp* migration from phosphorus to tungsten with a change in the coordination mode from η¹ to η⁵ (Scheme 1). This reaction proceeds primarily under thermolytic conditions, however, photolysis of **1** leads, additionally, to the elimination of a Cp* moiety and the formation of the radical intermediate **H**.^[24] The electronic structure of **H** was recently calculated by using DFT methods.^[21] We now find that this intermediate acts as a phosphorus radical transfer reagent and is responsible for the reaction of **1** with diphosphenes to afford an unprecedented complex of type **E**.

Photolysis of **1** in the presence of Mes*P=PMe₃* (Mes* = 2,4,6-tri-*tert*-butylphenyl) in toluene at 15 °C results in a color change from deep blue to greenish brown over a period of five hours, which indicated the completion of the reaction (Scheme 2). Separation of the crude reaction mixture by preparative TLC resulted in the isolation of a blackish green

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Supporting information for this article (full synthetic and spectroscopic details for **2-5**, and full details and references for the DFT calculations and the spectroelectrochemical investigations) is available on the WWW under <http://dx.doi.org/10.1002/anie.200805892>.



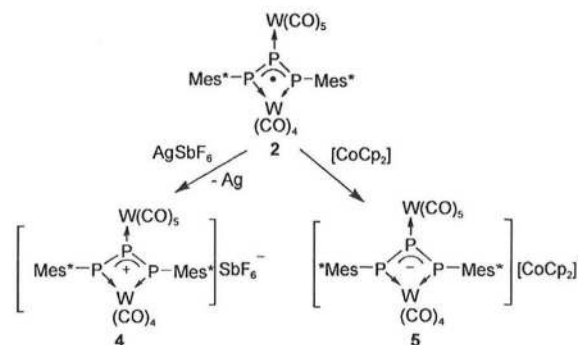
Scheme 2. Synthesis of the complexed triphosphaallyl radical

fraction, from which the radical species **2** was obtained as a black crystalline compound in 22% yield. Compound **3** was isolated from the second, blue fraction as a dark green crystalline compound in 35% yield. The ^{31}P NMR spectrum of the reaction mixture shows no signals that correspond to **3**, thus it seems that **3** was formed during the chromatography as a decomposition product of **2**. When the TLC plates were dried, hydrogen abstraction was prevented and the yield of isolated **2** increased to 40%, with only traces of **3** being produced. Since no thermal reaction between the starting materials occurs, the nucleophilic attack of the diphosphene at the electrophilic phosphinidene phosphorus atom can be excluded. Complex **2** is thus likely to be formed by addition of the photogenerated radical **H** to the P=P bond of the diphosphene, followed by a rearrangement.

Compounds **2** and **3** are readily soluble in hexane and CH_2Cl_2 , and give the expected IR spectroscopic and mass spectrometric data. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3** shows three doublets of doublets of an AMX spin system, each of which with a pair of tungsten satellites. The signal for the hydrogen bearing P atom is shifted upfield ($\delta = -62.4$ ppm) from the P atoms of the P=P bond ($\delta = 382.4$ and 450.6 ppm, $^1J(\text{P,P}) = 271$ Hz). Interestingly, all three signals in the ^{31}P NMR spectrum of **3** show an eight line pattern, which is attributed to the P H couplings.^[25] No NMR signal is observed for radical **2** because of the paramagnetic line broadening. The EPR spectrum of a solution of **2** in hexane at room temperature shows a six line signal that can be interpreted as doublets of a triplet at a g value of 2.0176. The ^{31}P hyperfine coupling constants are determined as 8.91 mT (terminal P atoms) and 2.11 mT (central P atom).^[25] Interestingly, the coupling constants derived for **2** are larger than the experimental values for the proposed derivative **D**,^[15] although, according to the calculations, the spin density in **D** should be located at the terminal P atoms, as in **2**.

The electrochemical behavior of **2** was studied by cyclic voltammetry.^[25] The voltammogram of **2** exhibits a reversible one electron oxidation to the corresponding cation at 0.17 V, and a reversible one electron reduction to the corresponding anion at -0.81 V. Spectroelectrochemical investigations show that the reduction of **2** leads to a shift of the carbonyl bands to lower wavenumbers. The values of the electrochemical potentials of **2** imply that AgSbF_6 and $[\text{CoCp}_2]$, respectively,

are suitable reagents for the oxidation and reduction of **2**.^[26] The reaction of **2** with one equivalent of AgSbF_6 in CH_2Cl_2 ($E^0 = +0.65$ V^[26]) at -78°C led to the oxidation product **4** (Scheme 3). This reaction was accompanied by a rapid color



Scheme 3. Oxidation and reduction of the complexed triphosphaallyl radical.

change from blackish green to deep purple and the appearance of a silver mirror. The ^{31}P NMR spectrum of the purple solution shows a AM_2 spin system with signals at $\delta = 586.5$ ppm ($^1J(\text{P,P}) = 250$ Hz, $^1J(\text{P,W}) = 272$ Hz) and $\delta = 344.5$ ppm ($^1J(\text{P,P}) = 250$ Hz, $^1J(\text{P,W}) = 267$ Hz), thus indicating the formation of a cation in which the two terminal P atoms of the P_3 unit are symmetry equivalent. The ESI mass spectrum of the reaction mixture of **4** shows the SbF_6^- ion at m/z 235 and the molecular ion peak of the cation at m/z 1203. We were not able to isolate **4** from the reaction mixture because of its rapid decomposition (within 30 minutes) at room temperature.

Treatment of **2** with stoichiometric amounts of $[\text{CoCp}_2]$ in CH_2Cl_2 ($E^0 = -1.33$ V^[26]) at -78°C resulted in the formation of the diamagnetic reduction product **5** (Scheme 3) as a green compound, which was isolated in 57% yield. All the signals in the A_2M type $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** are shifted upfield compared to those of **4** (P_A atom **4**: $\delta = 586.5$ ppm, **5**: $\delta = 468.5$ ppm; P_M atom **4**: $\delta = 344.5$ ppm, **5**: $\delta = 108.3$ ppm). The $^1J(\text{P,P})$ coupling constant increases from 250 Hz in **4** to 378 Hz in **5**, which reveal $^1J(\text{P,W})$ couplings of 207 Hz and 157 Hz, respectively.^[25] The IR absorptions for the CO ligands of **5** agree with those obtained upon reduction of **2** at -0.90 V under the in situ spectroelectrochemistry conditions.^[25] The large shifts of the $\{\text{W}(\text{CO})_4\}$ bands compared to those of the $\{\text{W}(\text{CO})_5\}$ moiety suggest that the terminal P1 units are more affected by reduction than the central atom P2 .

Single crystals of **2** were obtained at -25°C from its CH_2Cl_2 solution. In its crystalline state, radical **2** surprisingly showed no apparent decomposition, even in air at room temperature for several days. The molecular structure of **2**^[27] is shown in Figure 1 and reveals a Mes^* substituted phosphoallylic system, which is η^2 coordinated to a $\{\text{W}(\text{CO})_4\}$ unit by the phosphorus atoms P1 and $\text{P1}'$. The central atom of the three membered phosphorus chain P2 is η^1 coordinated to a $\{\text{W}(\text{CO})_5\}$ unit. The molecule has C_2 symmetry with the central unit, which consists of the seven atoms C6 , $\text{C6}'$, P1 , $\text{P1}'$, P2 , W1 , and W2 , situated within one plane. The $\text{P1/P1}'\text{-P2}$

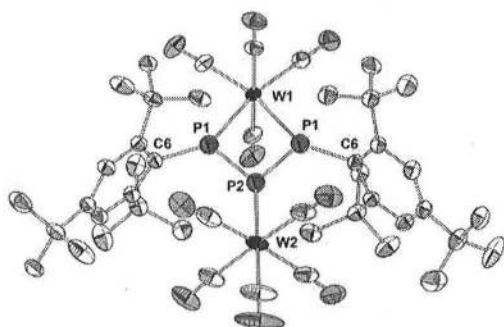


Figure 1. ORTEP representation of **2** (hydrogen atoms omitted for clarity, thermal ellipsoids set at 50% probability).

bond length (2.112(2) Å) is the average of a P–P bond (β P₄: 2.20 Å^[28]) and a P=P bond (the calculated bond length for H–P=P–H is 2.004 Å^[29]). These data suggest a bond order of 1.5, which is commonly found in allylic systems. The P1 P2 P1' angle (83.7(1)°) is diminished compared to that of an organic allylic system. The Mes* groups are twisted against the P1 P2 W1 W2 plane with a dihedral angle of 85.7(1)°, which prevents conjugation between the W₂P₃ system and the phenyl rings.

The molecular structure of **3** (Figure 2)^[27] reveals that protonation of **2** at the P1 atom distorts the coplanar arrangement of the P and W atoms. The P1–P2 bond length (2.187(3) Å) corresponds to a single bond, whereas the P2–P3 bond (2.075(3) Å) corresponds to a double bond.

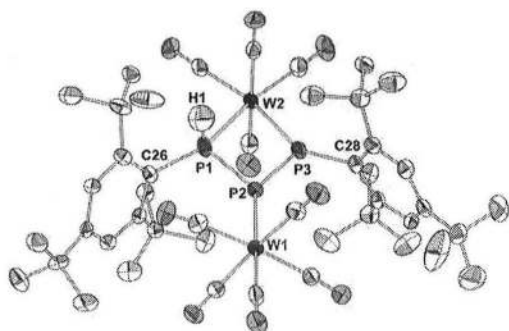


Figure 2. ORTEP representation of **3** (hydrogen atoms omitted for clarity, thermal ellipsoids set at 30% probability).

The cobaltocenium salt **5** crystallized from a CH₂Cl₂ solution. The experimental X ray structure of **5** (Figure 3)^[27] differs only slightly from the C₂ symmetric one (see DFT calculations). Deviations from ideal symmetry are probably due to packing effects in the presence of the counterion in the crystal lattice. The same behavior is also found for 2-CH₂Cl₂.^[25,27] In contrast to the radical **2**, the P–P bond lengths are shortened (P1–P2 2.070(3) Å, P2–P3 2.065(3) Å) in the anion of **5**, whereas the W–P bond lengths are elongated (W1–P1 2.568(2) Å, W1–P3 2.552(2) Å, W2–P2 2.492(2) Å). Additionally, the coplanar arrangement of the atoms C6, C6', P1, P1', P2, W1, and W2 atoms in **2** is distorted.

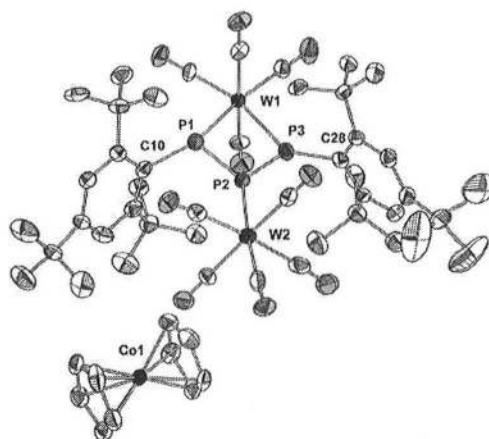


Figure 3. ORTEP representation of **5** (hydrogen atoms omitted for clarity, thermal ellipsoids set at 50% probability).

DFT calculations showed the energy minima for **2**, **4**, and **5** to be C₂ symmetric, which are lower in energy than their C_{2v} symmetric counterparts by 4.1, 4.5, and 16.3 kJ mol⁻¹, respectively. Selected calculated and experimental structure parameters of the central W2 (η¹)P₃(η²) W1 unit in **2**, **4**, and **5** are given in Table 1. The agreement between predicted and

Table 1: Comparison of selected theoretical and experimental structural parameters [Å,°] of **4**, **2**, and **5**.

Parameter	4		2		5 ^[a]	
	Calcd	Calcd	Calcd	Exp	Calcd	Exp
P1 W1 (P1' W1)	2.468	2.531	2.468(1)	2.615	2.568 (2.552)	
P2 W2	2.472	2.535	2.471(2)	2.590	2.492	
P1 P2 (P1' P2)	2.159	2.134	2.112(2)	2.110	2.070 (2.065)	
P1 C6 (P1' C6')	1.831	1.844	1.835(3)	1.870	1.855 (1.833)	
P1 P2 P1'	81.9	84.6	83.7(1)	88.99	88.70(10)	
P1 P2 P1' C6'	180.0	180.0	180.0	156.7	156.4(2) ^[b]	

[a] The atoms P1', C6, and C6' in **5** correspond to P3, C28, and C10, respectively, in Figure 3. [b] Value for the P3 P2 P1 C10 angle; the P1 P2 P3 C28 angle is 160.3(2)° (see Figure 3).

experimental values is good for the radical **2** and anion **5**, except for slightly overestimated P–W bond lengths. As a general trend, the increasing number of electrons in **4**, **2**, and **5** causes significant elongation of the P–W bond (the calculated difference between **4** and **5** is ca. 0.15 Å) and a slight contraction of the P–P bond lengths. The central ditungsten triphosphaallyl moiety in **2** and **4** remains coplanar with the C6/6' atoms and the difference between the C₂ and C_{2v} symmetric structures is merely a rotation of two *para tert* butyl groups of the Mes* substituents. Both P–C bonds in **5** are tilted about 23° from the plane of the W2 (η¹)P₃(η²) W1 unit.

The molecular orbital analysis of the central W2 (η¹)P₃(η²) W1 moiety in **2**, **4**, and **5** gives some insight into their bonding. The isosurface orbital plots of the π orbital system in the ditungsten triphosphaallyl unit of all three compounds is shown in Figure 4. In **2** and **4**, the orbitals 3b, 4a,

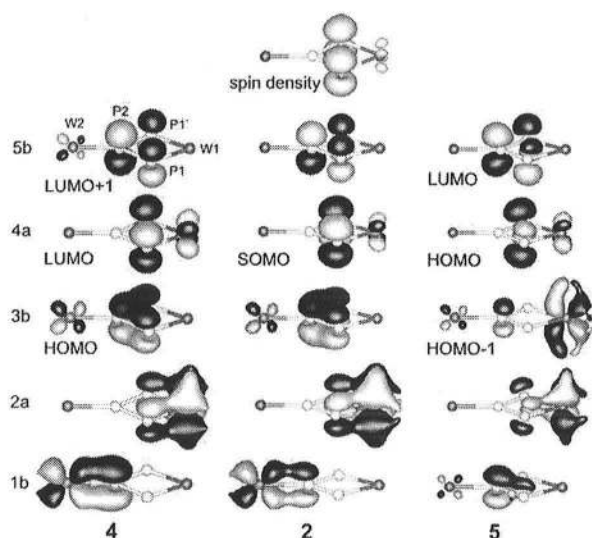


Figure 4. Isosurface orbital plots of the π system in the ditungsten triphosphaallyl unit in cation **4**, radical **2** (natural orbitals and spin density), and anion **5**. The orbitals are labeled by their numerical order and symmetry.

and **5b** closely resemble the classical π system of the C_3 allyl anion, radical, and cation, respectively. The shape of the **4a** orbital in **2** and the corresponding spin density explains the high spin densities at the terminal P atoms and agrees with the experimental EPR data. Additionally, the orbital picture also reveals a resonance stabilization of the central P_3 allyl moiety by an admixture of d orbitals of both W atoms. The **1b** orbital shown in Figure 4 is a $p(P2) d(W2)$ π bonding combination in **4** and **2**. In all three compounds, the **2a** and **4a** orbitals are bonding and antibonding combinations, respectively, of the $p(P1/1')$ and $d(W1)$ orbitals. The increasing occupation of the **4a** antibonding $p(P1/1')$ $d(W1)$ orbital from cation **4** to anion **5** results in a destabilization of the $p(P) d(W)$ orbital system and elongation of the P–W bonds. As a result of full occupation of the **4a** antibonding orbital, the orbital composition of anion **5** is different to those of **4** and **2**. The highest occupied molecular orbital (HOMO) of **5** is a doubly occupied antibonding $p(P1/1')$ $d(W1)$ orbital and HOMO–1 is a nonbonding combination of $p(P2)$ and $d(W1/2)$ orbitals. The π bonding combination of p orbitals of the P_3 group shifts significantly (2.2 eV) below the HOMO level (**1b** in Figure 4, see Ref. [25] for orbital energies), which explains the increased P–P bond strength and the shortening of the P–P bond distances along the series from the radical **2** to the anion **5**.

In summary, we have shown that the photolytic reaction of **1** with a diphosphene yields an unprecedented air stable triphosphaallyl radical $[(CO)_5W(\mu, \eta^2: \eta^1 P_3 Mes^*_2)W(CO)_4]$ (**2**). Oxidation of **2** leads to the triphosphaallyl cation (in compound **4**), which is only stable at low temperatures in solution, whereas upon reduction the stable triphosphaallyl anion (in compound **5**) is formed. Compounds **2**, **4**, and **5** represent the so far elusive redox congeners of the triphosphaallyl system. The frontier orbitals are indicative of a π allylic system that is partially resonance stabilized by the

d orbitals of both W atoms. The singly occupied molecular orbital (SOMO) and the corresponding spin density distribution of the radical **2** show that the unpaired spin is evenly distributed over both terminal P atoms; this is confirmed by EPR spectroscopy. The photogenerated phosphinidene radical **H** has been shown to be an excellent phosphorus radical transfer reagent and is thus valuable for future investigations into the generation of different open shell systems.

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- [27] The crystal structure analyses were performed on an OXFORD Diffraction Gemini R Ultra CCD diffractometer for **2** and **2-CH₂Cl₂** with MoK α radiation (λ 0.71073 Å) and for **3** and **5-2.5 CH₂Cl₂** with CuK α radiation (λ 1.54180 Å). The structures were solved by direct methods with the program SHELXS 97,^[30a] and full matrix least square refinement on F^2 in SHELXL 97^[30b] was performed with anisotropic displacements for non H atoms. Hydrogen atoms were located in idealized positions and refined isotropically according to the riding model. **2**: C₄₅H₅₈O₉P₃W₂, M_r 1203.50, crystal dimensions: 0.26 × 0.22 × 0.13 mm, monoclinic, space group $C2/c$, a 15.233(1), b 20.720(1), c 15.969(1) Å, β 95.350(11)°, T 123(1) K, Z 4, V 5018.2(7) Å³, ρ_{calcd} 1.593 g cm⁻³, μ 4.725 mm⁻¹, 27710 reflections collected, 5404 unique reflections (R_{int} 0.0272, $2\theta_{\text{max}}$ 53.80°), 269 parameters, R_1 0.0225, wR_2 0.0579; for **2-CH₂Cl₂**: C₄₆H₆₀O₉Cl₂P₃W₂, M_r 1288.43, crystal dimensions: 0.45 × 0.07 × 0.03 mm, monoclinic, space group $P2_1/c$, a 16.9423(9), b 11.1893(3), c 28.2800(15) Å, β 105.750(5)°, T 150(1) K, Z 4, V 5159.8(4) Å³, ρ_{calcd} 1.659 g cm⁻³, μ 4.701 mm⁻¹, 28905 reflections collected, 7804 unique reflections (R_{int} 0.0395, $2\theta_{\text{max}}$ 50.22°), 577 parameters, R_1 0.0408, wR_2 0.0875; **3**: C₄₅H₅₉O₉P₃W₂, M_r 1204.52, crystal dimensions: 0.129 × 0.076 × 0.042 mm, triclinic, space group $P1$, a 9.765(5), b 10.916(5), c 24.443(5) Å, α 80.883(5), β 80.772(5), γ 77.931(5)°, T 150(1) K, Z 2, V 2493.8(18) Å³, ρ_{calcd} 1.604 g cm⁻³, μ 9.709 mm⁻¹, 49135 reflections collected, 5352 unique reflections (R_{int} 0.0492, $2\theta_{\text{max}}$ 102.48°), 553 parameters, R_1 0.0329, wR_2 0.0846; **5-2.5 CH₂Cl₂**: C_{57.5}H₇₃O₉P₃W₂CoCl₅, M_r 1604.95, crystal dimensions: 0.35 × 0.06 × 0.03 mm, tetragonal, space group $P4_2/n$, a 30.031(1), b 30.031(1), c 14.586(1) Å, α β γ 90°, T 123(1) K, Z 8, V 13155.1(2) Å³, ρ_{calcd} 1.621 g cm⁻³, μ 11.238 mm⁻¹, 28824 reflections collected, 9891 unique reflections (R_{int} 0.0388, $2\theta_{\text{max}}$ 124.20°), 723 parameters, R_1 0.0498, wR_2 0.1113. CCDC 711409 (**2**) 711410 (**2-CH₂Cl₂**) 711411 (**3**) and 711412 (**5-2.5 CH₂Cl₂**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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