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Reaction of 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene with $[Re_2(CO)_8(CH_3CN)_2]$: Novel coordination modes of the 1,1′-diphosphaferrocene ligand

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Abstract

Reaction of 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene (**1**) with $[Re_2(CO)_8(CH_3CN)_2]$ afforded two trimetallic complexes in which the heterometallocene is ligated across the Re–Re bond. The structure of the complex having **1** bridging the $Re_2(CO)_8$ moiety through two P atoms was determined by X-ray diffraction and compared with those of analogous complexes with organic bridging bis-phosphines. The second complex obtained in this reaction presumably contains **1** acting as a (P,Fe) bridging ligand.
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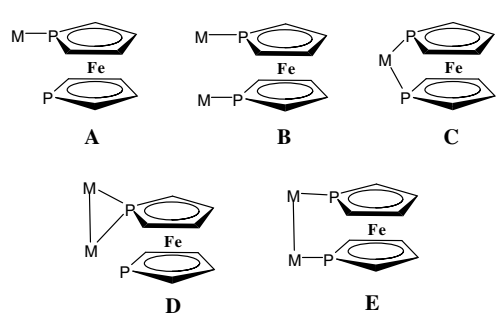
Keywords: 1,1′-Diphoshaferrocene; Rhenium carbonyl; Bridging ligand; X-ray structure

1. Introduction

1,1′-Diphosphaferrocenes, discovered by Mathey et al. [1], display rich coordination chemistry due to the presence of lone pairs of electrons at the phosphorus atoms [2–7]. In fact, the η^1-coordination to one and two metal centres (structures **A** and **B**, respectively), as well as the chelate coordination of both phosphorus atoms to one metal centre (structure **C**) and bridging of two-metal centres through one P atom (structure **D**) are well evidenced. Some of such complexes are efficient catalysts [7].



Logically, 1,1′-diphosphaferrocenes should also act as bidentate ligands spanning two directly bonded metal centres in metal clusters (structure **E**). This coordination mode, which is typical for organic bis-phosphines [8], along with unusual electronic properties [2] and redox-activity [9] would make 1,1′-diphosphaferrocenes very interesting ligands for chemistry of polynuclear complexes.

Attempts to obtain complexes of the type **E** in reaction of 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene (**1**) with bimetallic compounds $Co_2(CO)_8$ and $Mn_2(CO)_{10}$ failed, resulting only in the decomposition or formation of complexes of the type **A** or **B**, where M is a two-metal entity [2]. This failure has been tentatively explained by mismatch between the P–P distance in the *syn*-conformation of **1** and the **M**–**M** distance in the metal carbonyl backbone (the latter distance being markedly shorter). However, in light of theoretical calculations showing that the phosphorus-atom lone pairs in **1** have essentially spherical *s* character [7], which should enable adoption of this ligand to various geometries around metal centre(s) this argument does not seem justified.

In this communication, we report that reaction of **1** with the labile $[Re_2(CO)_8(CH_3CN)_2]$ complex leads to

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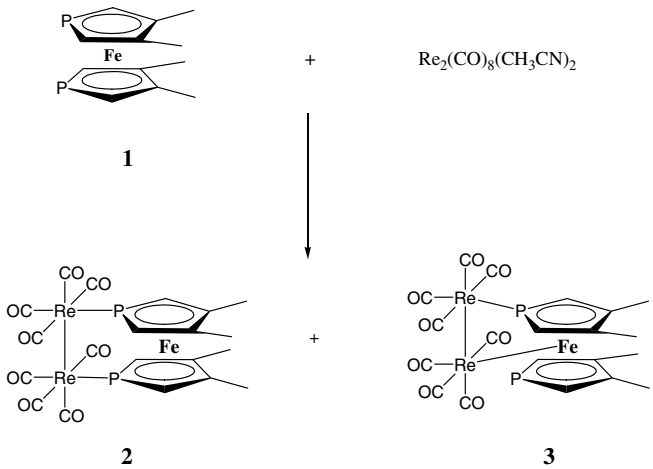
two complexes exhibiting unprecedented coordination modes of the 1,1′-diphosphaferrocene ligand to the bimetallic framework (P,P and presumably P,Fe bridging). Complex having **1** spanning two rhenium atoms through P atoms, was structurally characterized by single crystal X-ray diffraction.

2. Results and discussion

Reaction of **1** with $[Re_2(CO)_8(CH_3CN)_2]$ with **1** (molar ratio 1:1) was carried out in refluxing dichloromethane for 2 h. To reduce formation of expected oligomeric or polymeric compounds (**1** has two donor atoms and the rhenium complex two substitution-labile coordination sites), the reaction was carried out at a relatively low concentration of reactants. Column chromatography (SiO_2, hexane–chloroform 4:1) afforded yellow compounds **2** (16%) and **3** (34%). A substantial amount of deeply colored material (supposed to be a mixture of oligomers and polymers) was also formed and remained at the top of the column.



The ^{1}H NMR spectrum of **2** exhibits one signal (a doublet due to the coupling with ^{31}P) of four phospholyl protons and one signal of methyl protons, whereas its ^{31}P NMR spectrum shows a single resonance (−66.76 ppm). Its CI (methane) TOF mass spectrum shows the molecular ion and distribution of isotope peaks corroborating the suggested structure. The measured and calculated isotope pattern in the molecular peak of **2** are shown in Fig. 1.

The suggested molecular structure of **2** was confirmed by single crystal X-ray diffraction study (*vide infra*).

The ^{1}H NMR spectrum of the second isolated complex (Fig. 2) revealed nonequivalence of all phospholyl protons. Signals of the two of them appear as expected doublets, whereas those of two others display higher-order couplings. Besides these signals four methyl group resonances are observed. The ^{31}P NMR spectrum of this compound displays a broad signal at −53.6 ppm and a narrow singlet at −69.9 ppm. The complex gave practically the same elemental analysis data and CI TOF mass spectrum as **2** (the only difference was that in its mass spectrum an intense peak at *m/e* 278, (molecular mass of **1**) was observed). The IR spectra of both compounds reveal almost identical M−CO absorption band pattern (differing only in wavenumbers of particular bands), suggesting the same structure, $Re(CO)_4$–$Re(CO)_4$, of the metallocarbonyl backbone in both compounds.

The presented spectral and analytical data indicate that both compounds are composed of the $Re(CO)_4$–$Re(CO)_4$, moiety, containing two 16e Re(I) centers, ligating one molecule of **1**. This molecule should act as the four-electron ligand to ensure the stable 18e configurations of both Re atoms. Hence, both complexes may only differ in the mode of coordination of **1**. Recently, it was demonstrated that phosphaferrocenes can act as four-electron (P,Fe) ligands (the second pair of electrons is provided by the iron atom) [3]. We think that **1** can behave similarly and suggest that the second product of the reaction under study contain **1** ligated to the $Re(CO)_4$–$Re(CO)_4$ moiety through P and Fe atoms (structure **3**). According to ^{1}H NMR spectroscopy, solutions of **2** and **3** did not show any traces of interconvertion even after prolonged heating to 60 °C.

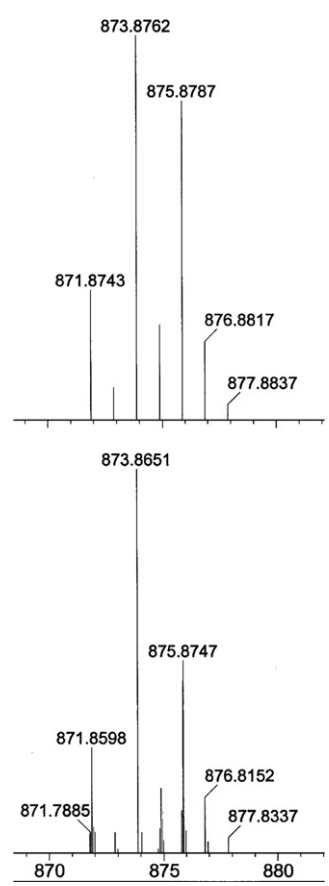


Fig. 1. Comparison of the measured (bottom) and calculated (top) isotope pattern in the molecular peak in the TOF-MS spectrum of **2**.

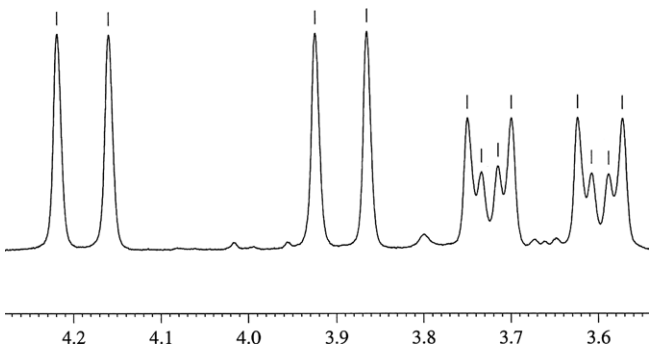
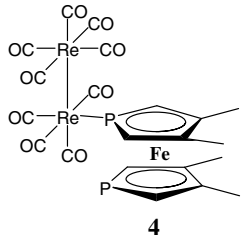


Fig. 2. Signals of the phospholyl protons in the 600 MHz ^{1}H NMR spectrum of **3** measured in $CDCl_3$.

Unfortunately, we were unable to obtain crystals of **3** suitable for X-ray crystallographic study to confirm this suggestion.

It was of interest to compare **3** with a more classical complex, bearing the $Re_2(CO)_9$ moiety bound to the one phosphorus atom in **1** in the η^1-fashion, **4**. We earlier prepared the complex having two $Re_2(CO)_9$ moieties bound to two phosphorus atoms of **1** in reaction of this complex with excess of $Re_2(CO)_{10}$ and Me_3NO [10]. Now, using the molar ratio of reactants ~1:1:1 we obtained **4** in 59% yield. The spectral and elemental analysis data fully confirmed the presented structure. The ^{1}H and ^{31}P NMR spectra of this compound show distinct signals of coordinated and non-coordinated phospholyl rings. The IR spectrum of **4** shows an absorption band at 2103 cm^{-1} characteristic for the $Re(CO)_5$ unit (the $Re(CO)_4$ units give rise to absorption bands in the 2065–2072 cm^{-1} region) [11]. We assume that the diphosphaferrocene ligand in **4** occupies an equatorial position of the $Re_2(CO)_9$ entity because the *eq,eq*-stereochemistry was established for the complex of **1** with two such entities [10].



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3. Molecular structure of 2

The molecular structure of **2** is shown in Figs. 3 and 4. Table 1 contains crystallographic data and structure refinement details and Table 2 selected bond distances and angles.

The structure clearly confirms the bridging coordination of **1** to the vacant equatorial sites of the $Re_2(CO)_8$ moiety. The molecule of **2** possesses a non-crystallographic C_2 symmetry with a pseudo twofold axis passing through Fe1 atom and the midpoint of the Re1–Re2 bond (Fig. 4). Two enantiomeric conformations of **2** coexist in the crystal. The geometry around each rhenium atom is best described as distorted octahedral with ligand–Re–ligand angles ranging from 85.7(5)° to 95.1(5)° and from 171.2(5)° to 176.9(4)°. The two rhenium octahedra are staggered being rotated from the eclipsed conformation by around 25° (e.g. the P–Re–Re–P torsional angle is 25.69(9)°). The P–P axis make a projection of 19.1(1)° onto the Re–Re bond. The phospholyl rings are planar and almost parallel with the dihedral angle equal to 2.57(1)°. These rings adopt a staggered conformation with the P11–Cg1–Cg2–P21 torsion angle of 17.0(2)°.

The length of the Re–Re bond in **2**, 3.095(1) Å is close to that found in the related complex with a classical diphosphine ligand, (Z)-$Ph_2PCH{=}CHPPh_2$, 3.079(1) Å [12], and bigger than that found in $Re_2(CO)_{10}$, 3.041(1) Å [13]. The $Re_2(CO)_8$-complexes with sterically more demanding bis-phosphines exhibit markedly longer Re–Re bonds (e.g. the Re–Re bond in the complex with 1,4-bis(diphenylphosphino)butane is 3.1791(2) Å) [14]. The striking difference between **2** and $Re_2(CO)_8$-complexes of organic bis-phosphines is that the P–P distance in the former, 3.279(6) Å is only slightly longer than the Re–Re bond, 3.0946(8) Å, whereas complexes with organic bis-phosphines show markedly bigger differences, e.g. the above mentioned complex of 1,4-bis(diphenylphosphino)butane shows the P–P distance 4.968 Å and the Re–Re distance 3.1791(2) Å [14]. This suggests that **1** is better adaptable to the geometry of the $Re_2(CO)_8$ backbone than organic bis-phosphines. It is also worthy noting than the P–P distance in **2** is significantly shorter than the sum of the Van der Waals radii of phosphorus atoms (3.6 Å) indicating the presence of a secondary bond between these atoms [15]. To the best of our knowledge this is the shortest P–P distance found for a derivative of **1**. The lengths of the Re–P bonds in **2**, 2.408(3) Å and 2.409(2) Å are the same as the analogous

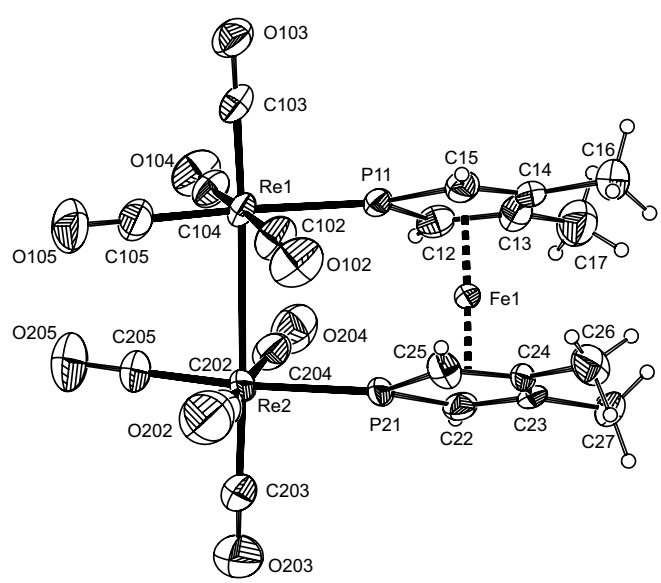

Fig. 3. Molecular drawing of **2** with atom-numbering scheme. Displacement ellipsoids are shown at 30% probability level.

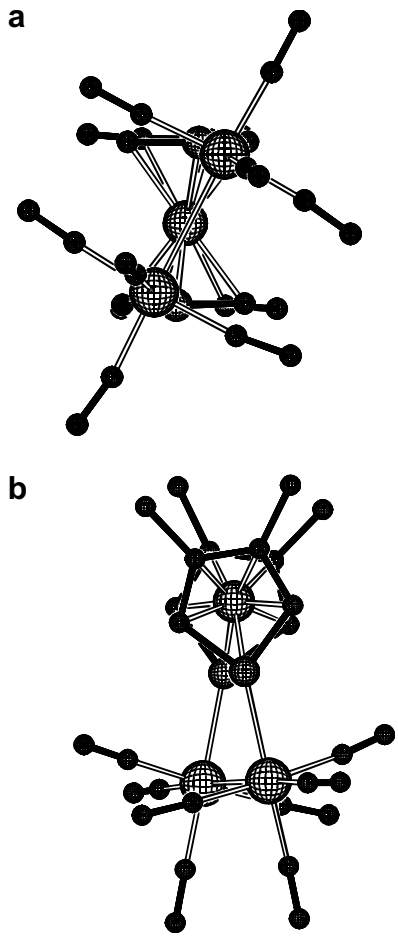

Fig. 4. Molecular conformation of **2**: a – view along pseudo twofold axis; b – view perpendicular to the phospholyl rings.

bonds in the η^1-complex of **1** with two $Re_2(CO)_9$ moieties, 2.4063(16) Å [10]. Therefore, the bridging coordination of **1** is not tighter than the η^1-coordination.

In conclusion, we have demonstrated that **1** likely organic bis-phoshines can be ligated across the Re–Re bond to the $Re_2(CO)_8$ moiety. The complex with bridging (P,P) **1** ligand displays several structural features different from those found in $Re_2(CO)_8$ – complexes with bridging organic bis-phosphines. It is likely that **1** will also act as a bridging ligand toward other bimetallic frameworks. In our opinion this finding opens an entry to the use of **1** and derivatives thereof in cluster chemistry.

4. Experimental

All reactions were carried out under argon. Solvents were distilled over appropriate drying agents thoroughly before use. Chromatographic separations were carried out on Silica gel 60 (Merck, 230–400 mesh ASTM). Complex **1** and $[Re_2(CO)_8(CH_3CN)_2]$ were prepared as described in the literature [16,17]. All other reagents are commercially available (Aldrich) and were used as received. NMR spectra were run on a Bruker AV 600 (600 MHz for ^1H) and a Varian Gemini 200BB (200 MHz for ^1H). IR spectra were recorded on a FT-IR Nexus spectrometer. CI(methane) TOF mass spectra were

Table 1
Crystallographic data and structure refinement details for **2**

Formula	$C_{20}H_{16}FeO_8P_2Re_2$
F_w	874.54
Crystal description	Purple block
Crystal size (mm)	0.2 × 0.2 × 0.3
Space group	$P2_1/n$
a (Å)	11.0818(7)
b (Å)	17.2063(11)
c (Å)	13.9630(5)
β (°)	112.923(6)
V (Å^3)	2452.2(3)
Z	4
d_x (g/cm^3)	2.366
Diffractometer	KUMA KM-4 CCD
Radiation type (λ) (Å)	Mo Kα (0.71073)
μ (mm^{-1})	10.592
Temperature (K)	293(2)
Data collected (h,k,l)	$-13 \leqslant h \leqslant 13$; $-20 \leqslant k \leqslant 20$; $-16 \leqslant l \leqslant 16$
θ range, (°)	2.99 – 25.00
Number of reflections measured	26151
Number of independent reflections	4325
R_{int}	0.0756
Number of reflections with $I > 2\sigma(I)$	3227
Solution	Direct methods
Refinement method	Full-matrix least squares on F^2
H atoms treatment	Constrained using rigid body model
Number of parameters	299
$R(F)$[a]	0.045 for $I > 2\sigma(I)$
$R(F)$[a]	0.070
$wR(F^2)$[b,c]	0.093 for $I > 2\sigma(I)$
$wR(F^2)$[b,c]	0.103
S	1.13
$(\Delta/\sigma)_{max}$	0.000
Difference in peak/hole (e/Å^3)	2.539/−3.675

[a] $R(F) = \sum(|F_o - F_c|)/\sum|F_o|$.
[b] $wR(F^2) = [\sum w(|F_o - F_c|)^2/\sum |F_o|^2]^{1/2}$.
[c] $w = 1/[\sigma^2(F_o^2) + (0.0417P)^2 + 1.5458P]$, where $P = [(F_o^2) + 2(F_c^2)]/3$.

Table 2
Selected bond distances (Å) and angles (°) in **2**

Re1–Re2	3.0946(8)
Re1–P11	2.408(3)
Re2–P21	2.409(2)
P11–Fe1	2.230(3)
P21–Fe1	2.226(4)
Cg1–Fe1	1.639(4)
Cg2–Fe1	1.632(4)
P11···P21	3.279(6)
P11–Fe1–P21	94.4(1)
P11–Re1–Re2	89.46(6)
P21–Re2–Re1	90.44(7)
Re1–P11–Cg1	174.6(1)
Re2–P21–Cg2	173.1(1)
P11–Re1–Re2–P21	25.69(9)
P11–Cg1–Cg2–P21	17.0(2)
Re1–Cg1–Cg2–Re2	20.7(2)

Cg1 and Cg2 corresponds to geometrical centres of P11–C12–C13–C14–C15 and P21–C22–C23–C24–C25 rings.

recorded on a Waters Micromass GCT spectrometer. Elemental analyses were performed by Service of Analyses CBMiM PAN (Łódź).

4.1. Reaction of 1 with $Re_2(CO)_8(CH_3CN)_2]$

Complex **1** (61 mg, 0.22 mmol) and $Re_2(CO)_8(CH_3CN)_2]$ (150 mg, 0.22 mmol) were refluxed in CH_2Cl_2 (250 ml) for 2 h. Evaporation to dryness and column chromatography (eluent: hexane–chloroform 8:2) afforded two fractions: (1) containing complex **3** (65 mg, 34%) and (2) containing compound **2** (27 mg, 16%).

Compound **3**: ^{1}H NMR (600 MHz, $CDCl_3$, δ): 4.19 (d, $J_{P-H} = 36.0$ Hz, 1H, α-phospholyl), 3.89 (d, $J_{P-H} = 36.0$ Hz, 1H, α-phospholyl), 3.72 (m, 1H, α-phospholyl) 3.59 (m,1H, α-phospholyl) 2.09, 2.06, 2.05, 2.02 (singlets, 3H each, Me's). ^{31}P NMR: −53.65(b, μ-P), −69.90 (noncoordinated P). IR ($CHCl_3$,cm^{-1}): 2085, 2000, 1977, 1907. Elemental Anal. Calc. for $C_{20}H_{16}FeP_2O_8Re_2$: C, 27.47; H, 1.84. Found: C, 27.50; H, 2.08%.

Compound **2**: ^{1}H NMR (600 MHz, $CDCl_3$, δ): 4.14 (d, $J_{P-H} = 33.0$ Hz, 4H, α-phospholyl) 1.89 (s, 12H, Me). ^{31}P NMR: −65.76. IR ($CHCl_3$, cm^{-1}): 2073, 2021, 1982, 1959, 1925. TOF MS Elemental Anal. Calc. for $C_{20}H_{16}FeP_2O_8Re_2$: C, 27.47; H, 1.84. Found: C, 27.63; H, 1.98%.

4.2. Synthesis of 4

To a solution of $Re_2(CO)_{10}$ (330 mg, 0.5 mmol) in THF (100 ml) Me_3NO (42 mg, 0.56 mmol) was added, the solution was stirred at r.t. for 30 min and concentrated to ~30 ml. Complex **1** (150 mg, 0.54 mmol) was then added and the solution was refluxed for 45 min. Evaporation to dryness and column chromatography (eluent: chloroform) afforded a small amount of unreacted **1** (first orange fraction) followed by yellow **4** (265 mg, 59%).

^{1}H NMR (200 MHz, $CDCl_3$, δ): 4.00 (d, $J_{P-H} = 35.9$ Hz, 2H, α-phospholyl), 3.61 (d, $J_{P-H} = 32.5$ Hz, 2H, α-phospholyl) 2.07 (s, 12 H, 4 × Me). ^{31}H NMR: −62.6 (broad s, coordinated P) −67.3 (d $J_{P-P} = 3.9$ Hz, noncoordinated P). IR (KBr,cm^{-1}): 2103, 2041, 1989, 1935. Elemental Anal. Calc. for $C_{21}H_{16}FeP_2O_9Re_2$: C, 27.95; H, 1.87. Found: C, 27.94; H, 1.87%.

4.3. X-ray structure determination of 2

Crystals of **2** suitable for X-ray analysis were obtained by slow diffusion of pentane into a concentrated solution of this compound in CH_2Cl_2. Crystallographic data were collected on KM-4 CCD area-detector diffractometer [18] using Mo Kα X-ray source. The unit cell dimensions were obtained from a least-squares fit to setting angles of 4516 reflections. A summary of X-ray details is given in Table 1. The structures was solved by direct methods using SHELXS 86 [19] and refined by full-matrix least square method using SHELXL 97 [20]. In the final step of refinement procedure, all non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with $U_{iso} = 1.2U_{eq}(C)$ for phosphacyclopenthadienyl ring H atoms or $1.5U_{eq}(C)$ for methyl groups.

Acknowledgement

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Appendix A. Supplementary material

CCDC 648093 contain 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.01.002.

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