Reactions of $[Re(NO)_2(PR_3)_2][BAr^F_4]$ complexes with phenylacetylene*

*C. M. Frech, A. Llamazares, M. Alfonso, H. W. Schmalle, and H. Berke**

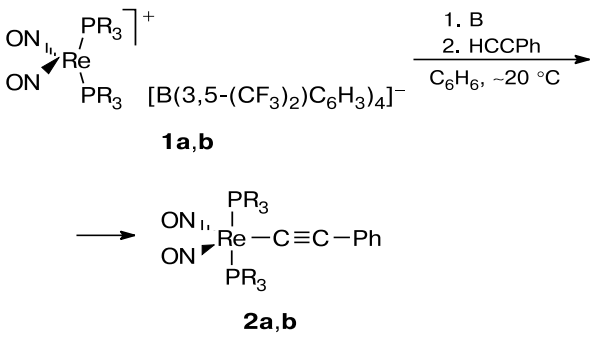
Department of Inorganic Chemistry, University of Zurich,
8057 Zurich, Switzerland.
E-mail: chfrech@aci.unizh.ch

The reaction of $[Re(NO)_2(PR_3)_2][BAr^F_4]$ (R = *cyclo*-C_6H_{13} (**1a**), Pr^i (**1b**); $[BAr^F_4]^-$ = $[B(3,5\text{-}(CF_3)_2C_6H_3)_4]$) with phenylacetylene in the presence of a non-nucleophilic base, like 2,6-bis(*tert*-butyl)pyridine (BTBP) or Bu^tOK, affords the phenylethynyl complexes $[Re(C{\equiv}CPh)(NO)_2(PR_3)_2]$ (R = *cyclo*-C_6H_{13} (**2a**); Pr^i (**2b**)) in moderate yields. In the absence of a base, complexes **1a** and **1b** are transformed into the compounds $[Re(C{\equiv}CPh)(CH{=}C(Ph)ONH)(NO)(PR_3)_2][BAr^F_4]$ (**3a** and **3b**, respectively). The structure of complex **3a** was confirmed by X-ray diffraction analysis. The latter reaction is proposed to be initiated by deprotonation of the terminal alkyne H atom by the bent nitrosyl ligand followed by the subsequent 1,3-dipolar addition of the ReN(H)O moiety to phenylacetylene.

Key words: rhenium, dinitrosyl complexes, phenylacetylene, alkynyl complexes, 1,3-dipolar addition.

A common method to prepare alkynyl complexes utilizes the reaction of transition metal complexes with terminal acetylenes. After coordination, the acetylenic C—H bond gets activated through oxidative addition[1] or σ-bond metathesis[2] to afford an alkynyl-hydride or an alkynyl complex. The subsequent rearrangement of the alkyne or the alkynyl-hydride species into a vinylidene compound is a very versatile transformation.[3] Several catalytic cycles have been proposed to involve the participation of the η^2-alkyne→η^1-vinylidene rearrangement.[4] In attempt to synthesize alkynyl (or vinylidene) complexes of the $[Re(NO)_2(PR_3)_2]^+$ fragment, these cationic species[5] were treated with phenylacetylene in the absence and presence of a base leading to different products.

Scheme 1



R = *cyclo*-C_6H_{13} (**a**), Pr^i (**b**)
B is base

Results and Discussions

Treatment of $[Re(NO)_2(PR_3)_2][B(3,5\text{-}(CF_3)_2C_6H_3)_4]$ (R = *cyclo*-C_6H_{13} (**1a**), R = Pr^i (**1b**)) with lithium phenylacetylide resulted in an inseparable mixture of yet unidentified products. When benzene solutions of complexes **1a** and **1b** were reacted with a large excess of phenylacetylene at room temperature in the presence of a non-nucleophilic base, like 2,6-bis(*tert*-butyl)pyridine (BTBP) or Bu^tO^-, new ^{31}P NMR signals appeared arising from the formation of alkynyl complexes (δ 21.7 for **2a** and δ 28.1 for **2b**) (Scheme 1). Concomitant decrease of the signals of **1a** and **1b** was observed. Complete conversion was achieved in few minutes indicated by a color change from dark red to orange-yellow. The ^1H and $^{13}C\{^1H\}$ NMR data are consistent with trigonal bipyramidal structures of $[Re(C{\equiv}CPh)(NO)_2(PR_3)_2]$ complexes with R = *cyclo*-C_6H_{13} (**2a**) and R = Pr^i (**2b**). Indeed, the $^{13}C\{^1H\}$ NMR spectra of **2a** and **2b** in C_6D_6 show at 20 °C C_α triplets at δ 128.7 for **2a** and at 128.9 for **2b** and C_β singlets at δ 118.0 (**2a**) and 118.2 (**2b**), in addition to the resonances assigned to the phenyl substituents of the phenylethynyl ligands (see Scheme 1). The IR spectra of both compounds exhibit two intense and characteristic bands at ~1610 and ~1570 cm^{-1} attributable to vibrations of two nitrosyl ligands. Additionally, weak bands were observed at $\nu \approx 2070$ cm^{-1} for both

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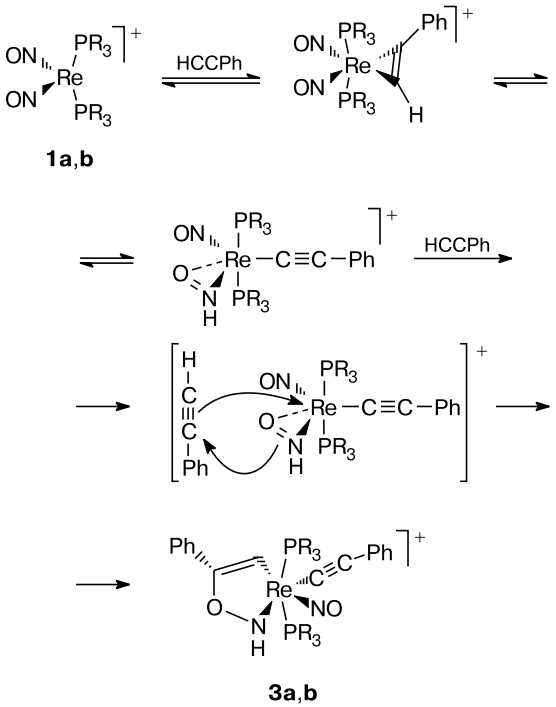
compounds due to the C≡C moieties.[6] Symmetric bond-stretching vibrations (a_{1g}) are expected to appear as strong bands in the solid state Raman spectra of the complexes. Indeed, they revealed an intense and characteristic emission at $\nu \approx 2075$ cm^{-1}, which confirms the presence of the C≡C unit. Alkynyl complexes **2** were isolated by extraction with pentane in moderate yields.

When the alkyne was added to benzene solutions of complexes **1** in the absence of a base, an unexpected cyclization reaction occurred involving one of the NO ligands, which confirms their high reactivity in such systems (Scheme 2, anions are not shown).*,**,[7] After the addition of the alkyne, a black oily precipitate was slowly formed. The reaction was completed within 30 min.

Scheme 2



1a,**b**

3a,**b**

R = *cyclo*-C_6H_{13} (**a**), Pr^i (**b**)

Monitoring the reaction course by ^{31}P NMR spectroscopy showed the formation of one major product. Unfortunately, attempts to isolate the compound in pure form were not successful. The $^{13}C\{^1H\}$ and ^1H NMR spectroscopic investigations in solution allowed structural assignments. The ^1H NMR spectra of **3a** and **3b** in THF-d_8 at 20 °C reveal in addition to the aromatic protons and those of the phosphine ligands a triplet at δ 8.94 and 9.08 for **3a** and **3b**, respectively, consistent with an *N*-protonated NO moiety.** In addition, small resonances in the olefinic region were observed. The $^{13}C\{^1H\}$ NMR spectrum demonstrates for both complexes the presence of aromatic carbon atoms and the phosphine ligands by additional triplets at δ 129.8 (**3a**) and 129.6 (**3b**), as well as singlets of very low intensity at δ 115.1 (**3a**) and 114.9 (**3b**), which were attributed to the ethynyl C atoms. The resonances for the three carbon atoms at δ 171.1, 129.6, and 114.9 correlate in a long range H—C correlation NMR experiment with the N—H proton of **3b**, which indicates the formation of an unsaturated cyclic (chelating) ligand including one of the nitrosyl ligands.

The IR spectra of these complexes show an intense and characteristic band for the remaining nitrosyl ligands at $\nu \approx 1710$ cm^{-1} and another one at $\nu \approx 1610$ cm^{-1} attributable to the HNO units and two weak absorptions at $\nu \approx 2240$ cm^{-1} and at $\nu \approx 2090$ cm^{-1}. The band at lower wavenumbers might be due to the C≡C moieties, while those at higher wavenumbers are due to (N—H) vibrations. The solid state Raman spectra of complexes **3a,b** exhibit a weak band at $\nu \approx 2090$ cm^{-1} corresponding to an a_{1g} vibration of the C≡C unit.[6]

However, based on these spectroscopic data, the structures of compounds **3** could not be assigned with certainty and, therefore, their structures were established by an exemplary X-ray diffraction study on a single crystal of **3a** (Fig. 1). Single crystals were grown by slow evaporation

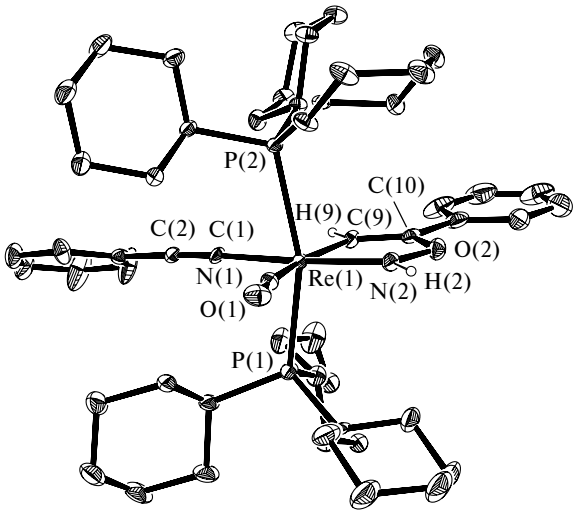


Fig. 1. Molecular structure of **3a** (20% probability displacement ellipsoids). Selected bond distances (Å): Re(1)—N(1) 1.809(7), N(1)—O(1) 1.173(8), Re(1)—C(1) 2.124(6), C(1)—C(2) 1.185(8), Re(1)—C(9) 2.095(7), C(9)—C(10) 1.317(8), C(10)—O(2) 1.392(8), O(2)—N(2) 1.345(7), Re—N(2) 1.988(5). Main bond angles (deg): N(1)—Re(1)—N(2) 93.5(3), N(2)—Re(1)—C(9) 73.5(2), C(9)—Re(1)—C(1) 91.3(3), N(1)—Re(1)—C(1) 101.7(3), Re(1)—N(1)—O(1) 171.3(5), Re(1)—N(2)—O(2) 123.0(4), Re(1)—C(9)—C(10) 116.9(5), C(9)—C(10)—O(2) 116.1(6), Re(1)—C(1)—C(2) 177.0(6). Counterion $[B(3,5\text{-}(CF_3)_2C_6H_3]^-$ and H atoms, except H(9) and H(2), were omitted for clarity.

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of a concentrated benzene solution at 25 °C. The rhenium center was found to be in a pseudo-octahedral environment with the alkynyl moiety and the remaining nitrosyl ligand in *trans*-arrangement. The C(1)—C(2) and Re(1)—C(1) distances are typical of an alkynyl moiety (1.185(8) and 2.124(6) Å, respectively). The C(9)—C(10) bond distance is 1.373(12) Å, clearly indicating double bond character and being consistent with the formation of the σ-*N*,*C*^{2}-(*O*-1-phenylethenylhydroxylamido-*C*^{2})yl ligand. The hydrogen H(2) atom was found in the difference Fourier map and refined isotropically.

The proposed mechanism for these unexpected reactions of **1a** and **1b** is depicted in Scheme 2. The initial reaction step is believed to be the formation of alkyne complexes. Interestingly enough that the following step requires a nitrosyl ligand to act as a base and thereafter the formed Re—N(H)—O moiety to act as a 1,3-dipole. This suggestion gains support from NMR studies of reacting compounds **1a** and **1b** with phenylacetylene at low temperatures in toluene-d_8. These studies reveal resonances consistent with the formation of π-acetylene intermediates. Raising the temperature to 25 °C afforded immediately **3a** and **3b** without further detectable intermediates. The reaction is accompanied by a color change from yellow to black. The increased acidity of the coordinated terminal alkyne group allows deprotonation with even weak bases. When no external base is present, phenylacetylene is deprotonated by a bent and therefore basic nitrosyl ligand, similar to the reaction of $[Re(H)(NO)_2(PR_3)_2]$ compounds with trifluoromethanesulfonic acid or HBF_4.* This HNO complex is then trapped by a second phenylacetylene molecule. Similarly to a 1,3-dipolar addition reaction, the Re—N(H)—O moiety adds to the acetylene to yield complexes **3a** and **3b** (see Scheme 2).

Thus, we have synthesized new rhenium phenylethynyldinitrosylbisphosphine complexes by the addition of phenylacetylene to the 16-electron $[Re(NO)_2(PR_3)_2]^+$ cations and deprotonation with a base. In the absence of a base, the alkyne complexes are deprotonated by one of the nitrosyl ligands, which initiates a cyclization reaction including a nitrosyl ligand and a second phenylacetylene molecule.

Experimental

All synthetic operations were conducted in oven-dried glassware using a combination of glovebox (MBRAUN 150B-G-II), high vacuum, and Schlenk techniques under dinitrogen atmosphere. The solvents were freshly distilled under N_2 according to standard procedures and were degassed by freeze—thaw cycles prior to use. Deuterobenzene, toluene-d_8, and THF-d_8 were purchased from Armar, stored in a Schlenk tube (Teflon tap), distilled over Na, and degassed prior to use. All the chemicals were purchased from Aldrich or Fluka. Unless otherwise stated, all reagents were used without further purification. Compounds $[Re(NO)_2(PR_3)_2][BAr^F_4]$ (**1**) were synthesized according to published procedures.[5]

Elemental analyses were performed on a Leco CHNS-932 analyzer at the University of Zurich, Switzerland. The ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker Avance DRX500 spectrometer. Chemical shifts are expressed in ppm referenced to C_6D_6 or THF-d_8. All chemical shifts for $^{31}P\{^1H\}$ NMR data are reported downfield in ppm relative to external 85% H_3PO_4 at 0.0 ppm. Processing and analyses of the spectra were done using the Bruker XWINNMR software. IR spectra were obtained by using KBr pellets with a Bio-Rad FTS-45 FTIR spectrometer. Raman spectra were recorded on a Renishaw Ramanscope spectrometer (λ_{exc} = 514 nm).

σ-Phenylethynyldinitroso-bis[tri(cyclohexyl)phosphine]rhenium(I) (2a) and σ-phenylethynyldinitroso-bis(triisopropylphosphine)rhenium(I) (2b). An excess of phenylacetylene was added to solutions of complexes **1** (80 mg) in benzene (10 mL) containing 1 equiv. of 2,6-bis(*tert*-butyl)pyridine at 25 °C accompanied by a color change from dark red to orange-yellow. After stirring the reaction mixture for ~15 min, the solvent was removed under reduced pressure. The product was extracted with pentane (3×10 mL) followed by filtration. The orange-yellow solution was dried *in vacuo*. The products can be recrystallized from a toluene—pentane mixture at −30 °C. The yields were 20.1 mg (53% for **2a**) and 21.2 mg (56% for **2b**).

Compound **2a**. Found (%): C, 57.81; H, 8.11; N, 2.94. $C_{44}H_{71}N_2O_2P_2Re$. Calculated (%): C, 58.19; H, 7.88; N, 3.08. IR, ν/cm^{-1}: 1571, 1609 (both s, NO); 2077 (w, C≡C). Raman, ν/cm^{-1}: 2079 (s, C≡C). ^1H NMR (C_6D_6, 25 °C), δ: 0.97—2.48 (m, 66 H, $P(C_6H_{11})_3$); 6.92—7.49 (m, C≡CPh). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C), δ: 26.8, 28.1, 30.3 (all s, $P(C_6H_{11})_3$); 36.5 (t, $P(C_6H_{11})$, $J_{P,C}$ = 10 Hz); 118.0 (s, C≡CPh); 128.7 (t, C≡CPh, $J_{P,C}$ = 20 Hz); 125.4, 126.1, 129.8, 135.4 (all s, C≡C(C_6H_5)). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C), δ: 21.7 (s, $P(C_6H_{11})_3$).

Compound **2b**. Found (%): C, 46.82; H, 7.29; N, 3.92. $C_{26}H_{47}N_2O_2P_2Re$. Calculated (%): C, 46.76; H, 7.09; N, 4.19. IR, ν/cm^{-1}: 1574, 1612 (both s, NO); 2072 (w, C≡C). Raman, ν/cm^{-1}: 2075 (s, C≡C). ^1H NMR (C_6D_6, 25 °C), δ: 1.25 (m, 36 H, $P\{CH\underline{Me}_2\}_3$); 2.49 (m, 6 H, $P\{C\underline{H}Me_2\}_3$); 6.96—7.45 (m, C≡CPh). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C), δ: 20.1 (s, $P\{CH(C\underline{H}_3)_2\}$); 26.8 (t, $P\{C\underline{H}Me_2\}$, $J_{P,C}$ = 12 Hz); 118.2 (s, C≡CPh); 128.9 (t, C≡CPh, $J_{P,C}$ = 20 Hz); 125.6, 126.3, 130.0, 135.8 (all s, C≡C(C_6H_5)). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C), δ: 28.1 (s, $P\{CHMe_2\}_3$).

κ^2-*N*,*C*^{2}-[*O*-(1-Phenylvinyl)hydroxylamido-*C*^{2}-yl]-σ-phenylethynyl-bis[tri(cyclohexyl)phosphine]rhenium(III) tetra[3,5-di(trifluoromethyl)phenyl]borate (3a) and κ^2-*N*,*C*^{2}-[*O*-(1-phenylvinyl)hydroxylamido-*C*^{2}-yl]-σ-phenylethynyl-bis[triisopropylphosphine]rhenium(III) tetra[3,5-di(trifluoromethyl)phenyl]borate (3b). A large excess of phenylacetylene was added to solutions of complexes **1** (50 mg) in benzene (10 mL), and the mixture was stirred for 30 min accompanied by the formation of a black oily precipitate. After removal of the solvent under reduced pressure, the residue was washed with pentane (3×10 mL) and dried *in vacuo*.

Compound **3a**. IR, ν/cm^{-1}: 1610 (m, HNO); 1716 (m, NO); 2089 (w, C≡C). Raman, ν/cm^{-1}: 2087 (s, C≡C). ^1H NMR (THF-d_8, 25 °C), δ: 0.87—2.53 (m, 66 H, $P(C_6H_{11})_3$); 5.06

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(br.s, 1 H, C<u>H</u>=C(Ph)ONH); 7.15—7.73 (m, 10 H, C≡C(C_6H_5), CHC(C_6<u>H</u>$_5$)ONH); 8.94 (t, 1 H, CH=C(Ph)ONH, $J_{P,C}$ = 2 Hz). $^{13}C\{^1H\}$ NMR (THF-d_8, 25 °C), δ: 27.0, 28.3, 30.4 (all s, P(C_6H_{11})$_3$); 36.2 (t, P(C_6H_{11})$_3$, $J_{P,C}$ = 10 Hz); 115.1 (br.s, <u>C</u>H=C(Ph)ONH); 129.8 (t, <u>C</u>≡CPh, $J_{P,C}$ = 20 Hz); 126.2, 129.0, 129.1, 129.2, 129.3, 130.6, 131.1, 131.7 (all s, C≡C(<u>C</u>$_6$H$_5$), CH=C(<u>C</u>$_6$H$_5$)ONH); 171.7 (s, CH=<u>C</u>(Ph)ONH). $^{31}P\{^1H\}$ NMR (THF-d_8, 25 °C), δ: 39.6 (s, P(C_6H_{11})$_3$).

<u>Compound **3b**</u>. IR, ν/cm^{-1}: 1610 (m, HNO); 1712 (m, NO); 2090 (w, C≡C). Raman, ν/cm^{-1}: 2074 (s, C≡C). ^{1}H NMR (THF-d_8, 25 °C), δ: 1.43 (m, 36 H, P{CH(C<u>H</u>$_3$)$_2$}$_3$); 2.68 (m, 6 H, P{C<u>H</u>Me$_2$}$_3$); 5.21 (s, 1 H, C<u>H</u>=C(Ph)ONH); 7.08—7.72 (m, 10 H, C≡C(C_6H_5), CHC(C_6<u>H</u>$_5$)ONH); 9.08 (t, 1 H, CH=C(Ph)ON<u>H</u>, $J_{P,C}$ = 2 Hz). $^{13}C\{^1H\}$ NMR (THF-d_8, 25 °C), δ: 20.1, 20.5 (both s, P{CH(<u>C</u>H$_3$)$_2$}$_3$); 28.4 (т, P{<u>C</u>HMe$_2$}$_3$, $J_{P,C}$ = 11 Hz); 114.9 (br.s, <u>C</u>H=C(Ph)ONH); 129.6 (br.s, <u>C</u>≡CPh); 126.6, 129.0, 129.1, 129.2, 130.5, 130.7, 131.1 (all s, C≡C(<u>C</u>$_6$H$_5$), CH=C(<u>C</u>$_6$H$_5$)ONH). $^{31}P\{^1H\}$ NMR (THF-d_8, 25 °C), δ: 43.5 (s, P{<u>C</u>HMe$_2$}$_3$).

X-ray diffraction study of complex 3a. A crystal of **3a** protected in hydrocarbon oil was selected for an X-ray experiment using a polarizing microscope. The crystal was mounted on a tip of a glass fiber and immediately transferred to the goniometer of an imaging plate detector system (Stoe IPDS diffractometer), where it was cooled to 183(2) K using an Oxford Cryogenic System. The crystal-to-image distance was set to 60 mm (θ_{max} = 27.99°). The ϕ-oscillation scan mode was applied for the intensity measurement. For the cell parameter refinement, 7998 reflections were selected out of the whole limiting spheres. A total of 44348 diffraction intensities were collected,[8] of which 20377 were independent (R_{int} = 0.0766) after data reduction. Numerical absorption correction[9] based on 15 crystal faces, was applied with the FACEitVIDEO and XRED programs.[8] The structure was solved by the Patterson method using the SHELXS-97 program package.[10] Interpretation of the difference Fourier maps, preliminary plot generations and checking for higher symmetry were performed with the PLATON program[11] and the implemented LEPAGE program.[12] All heavy atoms were refined (SHELXL-97)[13] using anisotropic displacement parameters. Positions of H atoms were calculated after each refinement cycle (riding model). The structural plot (see Fig. 1) was generated using the ORTEP program.[14] Other crystallographic data and the refinement results are presented in Table 1.

Table 1. Crystallographic data and structure refinement parameters for complex **3a**

Parameter	Value
Molecular formula	$C_{90}H_{96}BF_{24}N_2O_2P_2Re$
Crystal habitus	Plate
Color of crystals	Red
Crystal size/mm^3	0.45×0.36×0.16
Crystal system	Triclinic
Space group	$P\bar{1}$
T/K	183(2)
a/Å	12.6853(8)
b/Å	19.5877(14)
c/Å	21.0298(15)
α/deg	103.116(8)
β/deg	106.323(8)
γ/deg	105.106(8)
V/Å^3	4580.4(5)
Z	2
Molecular weight	1952.64
d_{calc}/g cm^{-3}	1.416
Absorption/mm^{-1}	1.457
F(000)	1984
Scan range, 2θ/deg	4.40—55.98
Number of collected reflections	44348
Number of independent relections	20377
Number of reflections with $I > 2\sigma(I)$	9693
Number of restraint parameters	48
Number of refinement parameters	1037
R_1/wR_2 ($I > 2\sigma(I)$)	0.0550/0.1154
R_1/wR_2 (all data)	0.1226/0.1307
Goodness of fit against F^2	0.769
Residual electron density/e·Å^{-3}, ρ_{max}/ρ_{min}	1.266/1.359

Supplementary crystallographic data for compound **3a** can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223 336033. E-mail: deposit@ccdc.cam.ac.uk).

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