

# Stepwise Formation of $\sigma$ -Alkynyl, Vinylidene, and Vinylphosphonium Complexes of Manganese(I)

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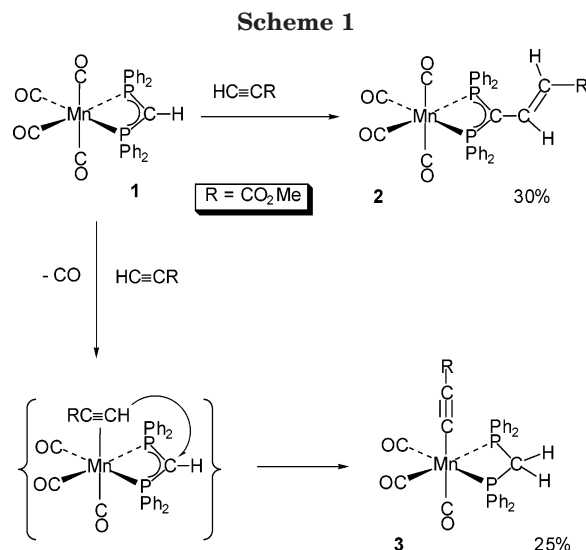
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**Summary:** Reaction of methyl propiolate with the diphosphinomethanide complex  $[\text{Mn}(\text{CO})_4\{\text{P}(\text{Ph}_2)_2\text{CH}\}]$  (**1**) produces simultaneously the insertion of the alkyne into the C–H bond, giving  $[\text{Mn}(\text{CO})_4\{\text{P}(\text{Ph}_2)_2\text{C}(\text{H})=\text{C}(\text{CO}_2\text{Me})\text{H}\}]$  (**2**), and the deprotonation of the alkyne mediated by the diphosphinomethanide ligand, affording the  $\sigma$ -alkynyl derivative  $\text{fac}[\text{Mn}(\text{C}\equiv\text{C}-\text{CO}_2\text{Me})(\text{CO})_3(\text{dppm})]$  (**3**). Protonation of **3** with  $\text{HBF}_4$  at 200 K affords the corresponding vinylidene compound  $\text{fac}[\text{Mn}(\text{C}=\text{C}(\text{H})-\text{CO}_2\text{Me})(\text{CO})_3(\text{dppm})]\text{BF}_4$  (**5**), which, on raising the temperature to 243 K, undergoes the spontaneous insertion of the vinylidene ligand into a Mn–P bond.

## Introduction

The chemistry of transition metal  $\sigma$ -alkynyl complexes has attracted much attention from organometallic chemists since a long time ago.<sup>1</sup> The special nature of the metal–carbon bond in these systems, the capability of transforming alkynyl complexes to other organometallic derivatives such as vinylidenes, and the fascinating properties of some alkynyl complexes, which range from optical nonlinearity to electrical conductivity, are the origin of that interest.<sup>2</sup> Transition metal  $\sigma$ -alkynyl complexes are usually prepared by reaction of halo complexes with alkynylating agents, such as alkynyl compounds of alkali metals, copper(I), or trimethylstannyl.<sup>2</sup> The synthesis of these complexes can also be carried out by direct reaction of the halo complexes with terminal alkynes, using an external base as deprotonating agent.<sup>3</sup> Interestingly, in a few cases deprotonation of the alkyne is achieved by a ligand of the starting complex acting as an internal base. This is the case in the hydride complexes  $[(\text{NP}_3)\text{RhH}]$  ( $\text{NP}_3$  = tetradentate ligand  $\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ ) and  $\text{cis}[\text{FeH}_2(\text{P}-\text{P})_2]$  ( $\text{P}-\text{P} = \text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2$ ;  $\text{R} = \text{Me}, \text{Et}, n\text{Pr}$ ), which react with phenyl acetylene to give the alkynyl complexes  $[(\text{NP}_3)\text{RhC}\equiv\text{CPh}]^4$  and  $\text{trans}[\text{Fe}(\text{C}\equiv\text{CPh})_2(\text{P}-\text{P})_2]$ ,<sup>5</sup> respec-



tively, through the elimination of  $\text{H}_2$ . In relation with this, here we describe the synthesis of the  $\sigma$ -alkynyl complex of manganese(I)  $\text{fac}[\text{Mn}(\text{C}\equiv\text{C}-\text{CO}_2\text{Me})(\text{CO})_3(\text{dppm})]$  by direct reaction of the diphosphinomethanide complex  $[\text{Mn}(\text{CO})_4\{\text{P}(\text{Ph}_2)_2\text{CH}\}]$  with methyl propiolate, which supposes an unprecedented way of forming  $\sigma$ -alkynyl derivatives. The stepwise transformation of this compound into vinylidene and vinylphosphonium derivatives is also described throughout this paper.

## Results and Discussion

Treatment of the diphosphinomethanide complex  $[\text{Mn}(\text{CO})_4\{\text{P}(\text{Ph}_2)_2\text{CH}\}]$  (**1**) with an excess of methyl propiolate in refluxing toluene gives a mixture of compounds  $[\text{Mn}(\text{CO})_4\{\text{P}(\text{Ph}_2)_2\text{C}(\text{H})=\text{C}(\text{CO}_2\text{Me})\text{H}\}]$  (**2**) and  $\text{fac}[\text{Mn}(\text{C}\equiv\text{C}-\text{CO}_2\text{Me})(\text{CO})_3(\text{dppm})]$  (**3**) in similar ratio (Scheme 1), which are separated by column chromatography. Compound **2** contains a vinyl-substituted diphosphinomethanide ligand resulting from the insertion of the alkyne into a  $\text{P}_2\text{C}-\text{H}$  bond of **1**, whereas the  $\sigma$ -alkynyl complex **3** can be assumed to be formed through substitution of a CO ligand by the alkyne followed by a deprotonation of the alkyne mediated by the diphosphinomethanide ligand (see Scheme 1).

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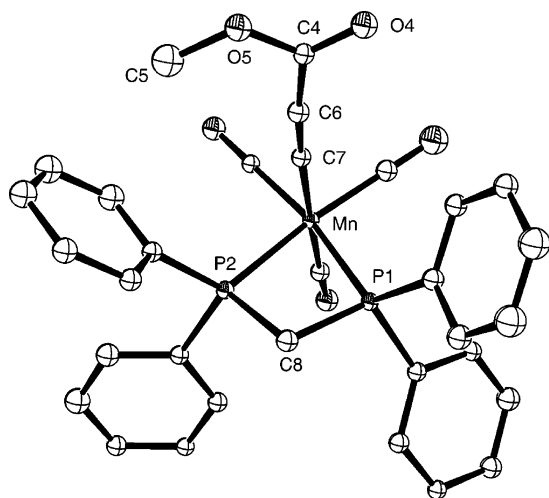
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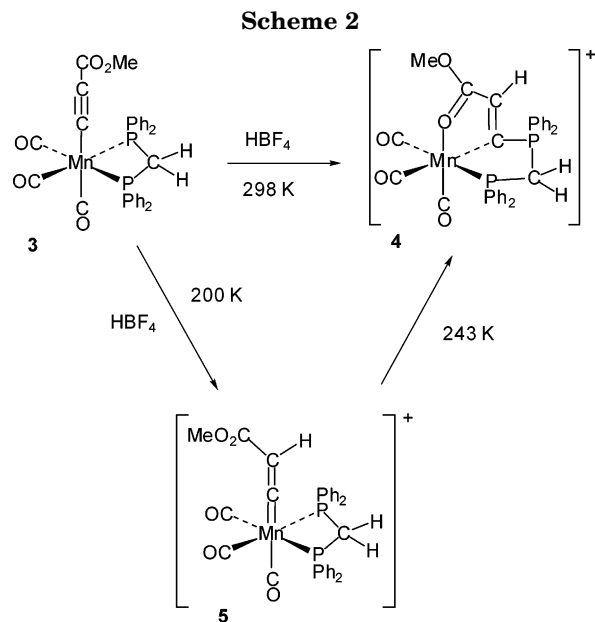


**Figure 1.** ORTEP drawing of compound **3**, showing only one of the two conformations adopted by the  $\text{CO}_2\text{Me}$  group. Hydrogen atoms are omitted for clarity. Selected bond distances ( $\text{\AA}$ ) and angles (deg):  $\text{C6}-\text{C7}$  1.208(2),  $\text{Mn}-\text{C7}$  1.980(2),  $\text{Mn}-\text{P1}$  2.3060(4),  $\text{Mn}-\text{P2}$  2.3165(4);  $\text{C7}-\text{C6}-\text{C4}$  173.6(2),  $\text{Mn}-\text{C7}-\text{C6}$  174.7(1),  $\text{P1}-\text{Mn}-\text{P2}$  72.84(2),  $\text{P1}-\text{C8}-\text{P2}$  95.51(7).

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **2** show resonances consistent with the alkenyl substituent on the diphosphinomethane ligand. Moreover, its nature is strongly supported by the X-ray structure elucidation of the closely related *fac*- $[\text{Mn}(\text{CN}t\text{Bu})(\text{CO})_3\{\text{P}(\text{Ph})_2\text{C}-\text{C}(\text{H})=\text{C}(\text{CO}_2\text{Me})\text{H}\}]$ , obtained as the sole product in the reaction of *fac*- $[\text{Mn}(\text{CN}t\text{Bu})(\text{CO})_3\{\text{P}(\text{Ph})_2\text{CH}\}]$  with methyl propiolate.<sup>6</sup> On the other hand, the IR spectrum of **3** exhibits a typical pattern for a *fac*-tricarbonyl complex in the  $\nu\text{CO}$  region (2016(vs), 1950(s), 1935(s)  $\text{cm}^{-1}$ ) together with a weak band corresponding to the  $\text{C}\equiv\text{C}$  stretching vibration (2093  $\text{cm}^{-1}$ ). The presence of the newly formed dppm ligand is corroborated by the  $^1\text{H}$  NMR spectrum of **3**, which gives signals for the two nonequivalent methylenic hydrogens in the appropriate region (4.80(m) and 4.37(m) ppm). The solid-state molecular structure of **3** was determined by X-ray analysis (Figure 1). The crystal structure reveals the presence of the alkyne ligand, with  $\text{C6}-\text{C7}$  (1.208(2)  $\text{\AA}$ ) and  $\text{Mn}-\text{C7}$  (1.9801(16)  $\text{\AA}$ ) bond lengths typical of a triple and single bond, respectively.<sup>7</sup> It is worth remarking that formation of **3** as described above represents a rare synthetic approach for  $\sigma$ -alkynyl derivatives from a terminal alkyne and a complex containing the deprotonating agent as a ligand (diphosphinomethane), which remains attached to the metal after proton abstraction (dppm).

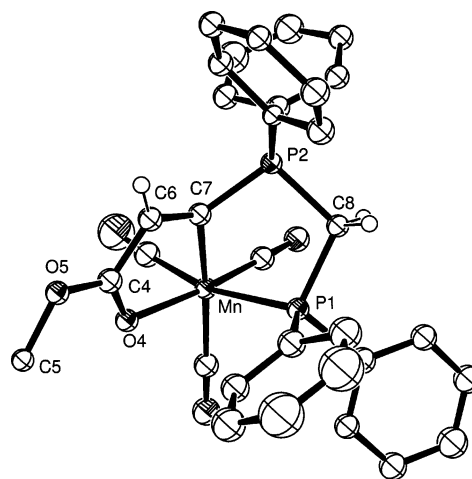
Efforts to extend this reaction to nonactivated terminal alkynes such as  $\text{HC}\equiv\text{CPh}$  have been unfruitful, because much decomposition occurs, and only an insignificant amount of the target  $\sigma$ -alkynyl derivative was spectroscopically detected in the reaction mixture.

Addition of 1 equiv of  $\text{HBF}_4$  to a solution of **3** in  $\text{CH}_2\text{Cl}_2$  at room temperature leads to the quantitative formation of **4** (Scheme 2). Complex **4** features a new



alkenyl phosphonium residue arising from the insertion of the vinylidene ligand into a manganese–phosphorus bond of the transient vinylidene complex **5**. This process leads to a coordination vacancy in the coordination sphere of the metal, which is occupied by the oxygen atom of the carboxylate group. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **4** displays two doublets (63.1 and 26.4 ppm,  $^2J(\text{PP}) = 34$  Hz) according to the presence of two nonequivalent phosphorus atoms. The  $^1\text{H}$  NMR spectrum shows a new doublet of doublets resonance (6.45 ppm,  $^3J(\text{PH}) = 25$ ,  $^4J(\text{PH}) = 7$  Hz) for the vinylic proton incorporated into the complex.

The structure of **4** was definitively elucidated by X-ray crystallography (Figure 2). The manganese atom is in an octahedral arrangement, being part of two fused five-membered metallacycles:  $\text{MnO}(4)\text{C}(4)\text{C}(6)\text{C}(7)$ , which is essentially planar, and  $\text{MnP}(1)\text{C}(8)\text{P}(2)\text{C}(7)$ , which is bent at manganese. The  $\text{C}(6)-\text{C}(7)$  bond length (1.342(3)  $\text{\AA}$ ) of the inserted vinylidene is in agreement with a double-bond character.



**Figure 2.** ORTEP drawing of the cationic complex **4**. Hydrogen atoms of phenyl and methyl groups are omitted for clarity. Selected bond distances ( $\text{\AA}$ ) and angles (deg):  $\text{C6}-\text{C7}$  1.342(3),  $\text{Mn}-\text{C7}$  2.033(2),  $\text{Mn}-\text{P1}$  2.3156(6),  $\text{Mn}-\text{O4}$  2.095(2);  $\text{C6}-\text{C7}-\text{P2}$  120.9(2),  $\text{Mn}-\text{C7}-\text{P2}$  119.0(1),  $\text{Mn}-\text{C7}-\text{C6}$  116.3(2),  $\text{P1}-\text{C8}-\text{P2}$  108.2(1).

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The intermediate vinylidene compound *fac*-[Mn(C=CH)(CO<sub>2</sub>Me)(CO)<sub>3</sub>(dppm)]BF<sub>4</sub> (**5**) (see Scheme 2), resulting from protonation of the alkynyl ligand, was not observed when performing the reaction at room temperature. However, the addition of HBF<sub>4</sub> at 200 K to a NMR sample of **4** instantaneously changes the color of the solution from yellow to red and allows spectroscopic detection of the vinylidene complex **5**. Thus the <sup>1</sup>H NMR spectrum showed the presence of the C=CH– proton as a new signal at 5.9 ppm, whereas the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum gave a singlet signal at 11.5 ppm, showing that phosphorus atoms remain equivalent. Below 243 K, **5** is the unique species detected, and above this temperature formation of **4** took place readily and quantitatively. Although a structure for **5** consisting of the η<sup>2</sup>-alkyne tautomer of the proposed vinylidene derivative cannot be totally excluded, it seems to be unlikely on the basis of similar results previously reported,<sup>13</sup> as well as considering the absence of P–H coupling in the C=CH– proton resonance.

Migratory insertion is an important reaction pathway for transition metal vinylidene complexes, with several examples being known of insertion of vinylidene ligands into metal–carbon σ-bonds,<sup>8</sup> and also into metal–nitrogen,<sup>9</sup> metal–oxygen,<sup>10</sup> and metal–halide bonds.<sup>11</sup> However, although a plethora of vinylidene complexes containing phosphines as ancillary ligands have been described, with some of them displaying important catalytic applications,<sup>12</sup> only a few examples of vinylidene insertion into a metal–phosphorus bond have been reported.<sup>13</sup> This phosphorus–carbon bond forming process is of great interest, as it represents a potential catalyst deactivation pathway for vinylidene complex-catalyzed organic transformations. It must be noted that related insertion of allenylidene<sup>14</sup> and alkyne<sup>15</sup> ligands into metal–phosphorus bond has been described recently.

There is no doubt that oxygen coordination is a driving force in the insertion reaction and product stabilization; thus insertion proceeds giving exclusively the *Z* alkenyl isomer, in which coordination through the carboxylate fragment is allowed. In fact, when trying to perform the vinylidene formation and subsequent vinylphosphonium stabilization by protonation reaction of σ-alkynyl complexes lacking carboxylate substituents as in *fac*-[Mn(C≡CPh)(CO)<sub>3</sub>(dppm)], only decomposition products were observed.

In conclusion, up to three rare reaction pathways are observed in the treatment of the diphosphinomethanide complex **1** with methyl propiolate: insertion of the

alkyne into a C–H bond, formation of a σ-alkynyl complex by intramolecular alkyne deprotonation, and insertion of a vinylidene ligand into a metal–phosphorus bond.

## Experimental Section

**General Remarks.** All reactions and manipulations were performed under a atmosphere of dry nitrogen by using standard Schlenk techniques. Solvents were distilled over appropriate drying agents under dry nitrogen prior to use. Compound [Mn(CO)<sub>4</sub>{(PPh<sub>2</sub>)<sub>2</sub>CH}] (**1**) was prepared as described elsewhere.<sup>16</sup>

**Synthesis of 2 and 3.** A solution containing **1** (0.20 g, 0.364 mmol) and methyl propiolate (162 μL, 1.82 mmol) in toluene (20 mL) was stirred at reflux temperature for 5 h. The color changed from yellow to red. The solvent was then evaporated to dryness and the remaining solid chromatographed through an alumina column (activity degree III). Elution with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:1) allowed the separation of compound **2** (0.069 g, 30%) from the first band (yellow) and compound **3** (0.055 g, 25%) from the second band (yellow). **2**: Anal. (%) Calcd for C<sub>33</sub>H<sub>25</sub>MnO<sub>6</sub>P<sub>2</sub>: C 62.47, H 3.97. Found: C 62.13, H 4.12. IR (CH<sub>2</sub>Cl<sub>2</sub>): ν 2076 (s), 1995 (vs), 1967 (m) cm<sup>-1</sup> (CO). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.83–7.46 (21H, m), 4.84 (1H, d, <sup>3</sup>J<sub>HH</sub> = 14), 3.60 (3H, s). <sup>31</sup>P{<sup>1</sup>H} NMR (121.5 MHz, CDCl<sub>3</sub>): δ 2.8 (br). **3**: Anal. (%) Calcd for C<sub>32</sub>H<sub>25</sub>MnO<sub>5</sub>P<sub>2</sub>: C 63.38, H 4.16. Found: C 63.56, H 4.28. IR (CH<sub>2</sub>Cl<sub>2</sub>): ν 2093 (w) cm<sup>-1</sup> (C≡C), 2016 (vs), 1950 (s), 1935 (s) cm<sup>-1</sup> (CO). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.71–7.20 (20H, m), 4.84 (1H, m), 4.37 (1H, m), 3.22 (3H, s). <sup>31</sup>P{<sup>1</sup>H} NMR (121.5 MHz, CDCl<sub>3</sub>): δ 21.6 (br).

**Synthesis of 4.** To a solution of **3** (0.05 g, 0.082 mmol) in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> was added tetrafluoroboric acid/diethyl ether complex (54%, 15 μL, 0.109 mmol) with stirring. The solvent was then evaporated, and the oil obtained was washed with diethyl ether (3 × 5 mL). Recrystallization in CH<sub>2</sub>Cl<sub>2</sub>/hexane provided **4** as yellow crystals; yield 0.057 g (90%). Anal. (%) Calcd for C<sub>32</sub>H<sub>25</sub>MnO<sub>5</sub>P<sub>2</sub>: C 55.36, H 3.77. Found: C 55.54, H 3.65. IR (CH<sub>2</sub>Cl<sub>2</sub>): ν 2033 (vs), 1966 (s), 1918(s) cm<sup>-1</sup> (CO). <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.99–7.40 (20H, m), 6.45 (1H, dd, <sup>3</sup>J<sub>PH</sub> = 25, <sup>4</sup>J<sub>PH</sub> = 7, C=CH), 5.40 (1H, ddd, <sup>2</sup>J<sub>PH</sub> = 16, <sup>2</sup>J<sub>PH</sub> = 10, <sup>2</sup>J<sub>HH</sub> = 5, CH<sub>2</sub>), 3.90 (1H, td, <sup>2</sup>J<sub>PH</sub> = 15, <sup>2</sup>J<sub>HH</sub> = 5, CH<sub>2</sub>), 3.59 (3H, s, CO<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121.5 MHz, CDCl<sub>3</sub>): δ 63.5 (d, <sup>2</sup>J<sub>PP</sub> = 34, MnPPh<sub>2</sub>), 26.4 (d, <sup>2</sup>J<sub>PP</sub> = 34, PPh<sub>2</sub>).

**NMR Detection of 5.** To a NMR sample of **3** (0.02 g, 0.033 mmol) in CD<sub>2</sub>Cl<sub>2</sub> was added tetrafluoroboric acid/diethyl ether complex (54%, 10 μL, 0.109 mmol) at 200 K. Keeping a low temperature, NMR experiments were performed. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.50 (20H, br), 5.90 (1H, br, C=C(H)(CO<sub>2</sub>Me)), 4.85 (2H, m, P<sub>2</sub>CH<sub>2</sub>), 3.18 (3H, br, CO<sub>2</sub>CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (161.99 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 11.48 (s, (PPh<sub>2</sub>)<sub>2</sub>).

**Crystallography.** Diffraction data were collected on an Enraf-Nonius KappaCCD diffractometer at 100 K. The structures were solved by direct methods and refined using full-matrix least-squares on *F*<sup>2</sup> with all non-hydrogen atoms anisotropically refined. Crystal data for **3** (C<sub>32</sub>H<sub>25</sub>MnO<sub>5</sub>P<sub>2</sub>): *M*<sub>r</sub> = 604.4, triclinic, space group *P*1̄, *a* = 9.50925(1) Å, *b* = 17.3418(2) Å, *c* = 18.1765(2) Å, α = 69.7090(5)°, β = 88.5567(5)°, γ = 89.6242(5)°, *V* = 2810.52(5) Å<sup>3</sup>, *Z* = 4, ρ<sub>calcd</sub> = 1.433 g/cm<sup>-3</sup>, *F*(000) = 1248, Mo *K*α radiation (λ = 0.71073 Å)<sub>air</sub>, crystal dimensions 0.36 × 0.24 × 0.20 mm. For 9477 reflections with [*I* > 2σ(*I*)] *R* indices: *R*1 = 0.0320 and *wR*2 = 0.0939. For all 11005 unique reflections *R* indices: *R*1 = 0.0394 and *wR*2

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= 0.1016. Crystal data for **4** ( $C_{32}H_{26}BF_4MnO_5P_2$ ):  $M_r = 694.22$ , monoclinic, space group  $P2_1/c$ ,  $a = 10.2407(2)$  Å,  $b = 16.6566(4)$  Å,  $c = 18.3683(4)$  Å,  $\beta = 95.650(1)^\circ$ ,  $V = 3117.96(12)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.479$  g/cm<sup>-3</sup>,  $F(000) = 1416$ , Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å), crystal dimensions  $0.44 \times 0.24 \times 0.20$  mm. For 4655 reflections with  $[I > 2\sigma I]$   $R$  indices:  $R1 = 0.0373$  and  $wR2 = 0.0945$ . For all 5480 unique reflections  $R$  indices:  $R1 = 0.0472$  and  $wR2 = 0.1010$ .

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**Supporting Information Available:** Crystallographic data of **3** and **4** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>. OM050146C