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Equilibrium Study of $Pd(dba)_2$ and $P(OPh)_3$ in the Pd-Catalyzed Allylation of Aniline by Allyl Alcohol

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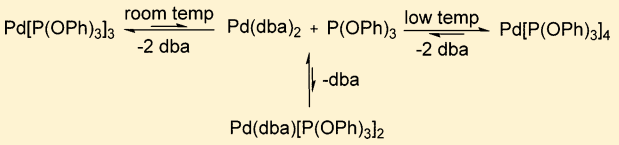
Supporting Information

ABSTRACT: Reaction of $Pd(dba)_2$ and $P(OPh)_3$ shows a unique equilibrium where the $Pd[P(OPh)_3]_3$ complex is favored over both $Pd(dba)[P(OPh)_3]_2$ and $Pd[P(OPh)_3]_4$ complexes at room temperature. At a lower temperature, $Pd[P(OPh)_3]_4$ becomes the most abundant complex in solution. X-ray studies of $Pd[P(OPh)_3]_3$ and $Pd(dba)[P(OPh)_3]_2$ complexes show that both complexes have a trigonal geometry with a Pd−P distance of 2.25 Å due to the π-acidity of the phosphite ligand. In solution, pure $Pd(dba)[P(OPh)_3]_2$ complex equilibrates to the favored $Pd[P(OPh)_3]_3$ complex, which is the most stable complex of those studied, and also forms the most active catalytic species. This catalyst precursor dissociates one ligand to give the reactive $Pd[P(OPh)_3]_2$, which performs an oxidative addition of nonmanipulated allyl alcohol to generate the π-allyl-$Pd[P(OPh)_3]_2$ intermediate according to ESI-MS studies.



The palladium-catalyzed allylic substitution via a π-allylpalladium intermediate, known as the Tsuji−Trost reaction, is one of the most powerful methods for constructing carbon−carbon and carbon−heteroatom bonds in organic synthesis (Scheme 1).[1]

Scheme 1. Palladium-Catalyzed Allylic Amination with Allyl Substrates

The reaction has been carried out using palladium and various allyl sources such as halides,[2a] esters,[2b,c] ethers,[2d] and carbonates.[2e] The direct catalytic substitution of allyl alcohol has recently attracted considerable attention for its environmental and economic advantages.[3] However, it is generally difficult to cleave the C−O bond because of the poor leaving group ability of the hydroxyl group.[4] The palladium-catalyzed direct substitution of allyl alcohols generally requires activation by a Lewis acid.[4,5] Recently, palladium complexes bearing strong π-acceptor ligands (bisphosphaalkene and triphenylphosphite)[6] have been reported to achieve the transformation without the use of activators. In 2004 Ikariya reported that $Pd[P(OPh)_3]_4$ catalyzed the direct allylic substitution of allyl alcohol by various nucleophiles. The catalyst was generated either from $PdCl_2(MeCN)_2$ in the presence of NEt_3 and $P(OPh)_3$ or *in situ* from tris(dibenzylideneacetone)dipalladium(0) $[Pd_2(dba)_3]$ and $P(OPh)_3$ in a 1:4 molar ratio.[6c]

The air-stable palladium(0)complexes $[Pd_2(dba)_3]$ and bis(dibenzylideneacetone)palladium(0) $Pd(dba)_2$ have been used as convenient sources of Pd(0) in palladium-catalyzed reactions.[7] Amatore and Jutand have in several studies shown that the dba (*E*-dibenzylidene acetone) ligand is not as labile as expected in a mixture of $Pd(dba)_2$ and triphenylphosphine (PPh_3) ligand (eq 1).[8] For a complete dissociation of dba, 50 equiv of PPh_3 to Pd was required according to UV spectroscopy. Interestingly, the electronic property of the phosphorus-based ligand has a profound effect on the equilibrium.[9] When 1-phenyldibenzophosphole (DBP) was used as ligand, the equilibrium is shifted opposite, in favor of $Pd(DBP)_4$, which was slower to initiate an oxidative addition reaction than the $Pd(dba)(DBP)_2$ complex.[10] Several examples of $Pd(dba)L_n$ (n = 1, 2) complexes of dba and phosphorus ligands have been isolated and characterized.[11]

$$Pd(dba)(PPh_3)_2 + PPh_3 \leftrightarrows Pd(PPh_3)_3 + dba \quad (1)$$

The reactivity of pure and *in situ* generated complexes may differ. For example, the oxidative addition of phenyl iodide by a mixture of $Pd(dba)_2$ and 4 equiv of PPh_3 proceeded at an overall rate 10 times lower than for isolated $Pd(PPh_3)_4$.[8a] In addition, several research groups have observed that *in situ* prepared $Pd(dba)(PPh_3)_2$ shows a higher reactivity in certain reactions than both *in situ* prepared and isolated $Pd(PPh_3)_4$.[8a,12] Mechanistic studies, including ESI-MS experiments, have shown that the dba ligand may act as a ligand in the Heck reaction.[13] In the catalytic procedure developed by Ikariya using *in situ* prepared $Pd[P(OPh)_3]_4$, different palladium species may be present in the reaction mixture (eq 2). We were interested in how the electron-deficient triphenylphosphite ligand would affect the equilibrium as compared to PPh_3 and DBP. We were

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also interested in investigating whether $Pd(dba)[P(OPh)_3]_2$ or $Pd[P(OPh)_3]_4$ is the most efficient precursor to generate the active catalytic species in an allylation of unactivated allyl alcohol and to determine whether $Pd[P(OPh)_3]_2$ or $Pd(dba)P(OPh)_3$ is the active catalyst. To our knowledge, the corresponding study performed by Jutand and Amatore has not been performed on π-acidic triphenylphosphite ligands. Taking into account the importance of such ligands in the allylation of unactivated allyl alcohols motivated us to study this equilibrium.[14]

$$Pd(dba)_2 + 4L \rightleftharpoons Pd(dba)L_2 \rightleftharpoons PdL_4 + 2dba \quad (2)$$

$$L = P(OPh)_3$$

An interesting difference between the triphenylphosphine and triphenylphosphite complexes of palladium was the number of ligands coordinated to the metal. In the phosphine palladium complex either three or preferably four ligands are coordinated to the palladium in $Pd(PPh_3)_3$ or $Pd(PPh_3)_4$, respectively. In contrast, the triphenylphosphite palladium complex has only three ligands coordinated to the palladium in $Pd[P(OPh)_3]_3$ (*vide infra*) at room temperature. To study the equilibrium between $Pd(dba)_2$ and triphenylphosphite $P(OPh)_3$, $Pd(dba)_2$ and the $P(OPh)_3$ were mixed at different concentrations and analyzed by ^{31}P NMR spectroscopy (Figure 1). At a 1:2 ratio between $Pd(dba)_2$ and $P(OPh)_3$, a 1:3 ratio between $Pd(dba)[P(OPh)_3]_2$ and $Pd[P(OPh)_3]_3$ was observed. The ^{31}P NMR spectrum of the mixture of $Pd(dba)_2$ with 2 equiv of $P(OPh)_3$ shows three signals (Figure 1d): one signal at δ 138.8 ppm, which was characteristic of $Pd[P(OPh)_3]_3$, as shown in Figure 1b, and two broad signals ($\Delta\nu_{1/2}$ = 61 Hz) of equal magnitude at δ 137.6 and 133.4 ppm, which correspond to the two nonequivalent phosphorus atoms in $Pd(dba)[P(OPh)_3]_2$, as shown in Figure 1c. This was different compared to the corresponding study using PPh_3, in which only the corresponding $Pd(dba)[PPh_3]_2$ complex was observed at the same ratio.[8] At a 1:4 ratio between $Pd(dba)_2$ and $P(OPh)_3$, broadening of the signals in the ^{31}P NMR spectrum was observed (Figure 1e). Unfortunately, the broadened signals could correspond to either $Pd[P(OPh)_3]_3$ (Figure 1b), $Pd(dba)[P(OPh)_3]_2$ (Figure 1c), free $P(OPh)_3$ (Figure 1a), or a new complex and were therefore difficult to interpret. Above 8 equiv of $P(OPh)_3$ to Pd, only one broadened signal in the ^{31}P NMR spectrum at δ 130.0 ppm was observed (Figure 1f). A similar spectrum was observed when isolated $Pd[P(OPh)_3]_3$ and $P(OPh)_3$ were mixed.

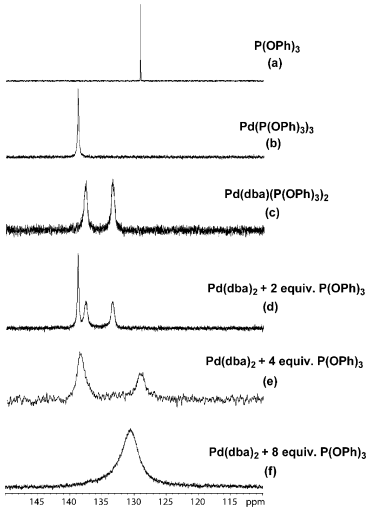

Figure 1. $^{31}P\{^1H\}$ NMR spectra (121 MHz) performed in 0.6 mL of C_6D_6 with H_3PO_4 as an external standard: (a) $P(OPh)_3$ (b) $Pd[P(OPh)_3]_3$, (c) $Pd(dba)[P(OPh)_3]_2$, (d) $Pd(dba)_2$ (15 mM) + $P(OPh)_3$ (30 mM), (e) $Pd(dba)_2$ (15 mM) + $P(OPh)_3$ (60 mM), (f) $Pd(dba)_2$ (15 mM) + $P(OPh)_3$ (120 mM).

The broadened signals observed at a 1:4 ratio between $Pd(dba)_2$ and $P(OPh)_3$ could have different explanations (*vide supra*). Therefore, the probe was cooled and the temperature effect of the equilibrium was studied by ^{31}P NMR spectroscopy. At −20 °C the two signals separated to give two chemical shifts at δ 127.2 and 138.5 ppm (Figure 2). At this temperature, both signals were sharper than at room temperature. The ratio of the integral of the two chemical shifts shifted from 7:3 (at 20 °C in favor of the signal at δ 138.5 ppm) to 1:1 at −20 °C. At −40 °C the signal at δ 127.2 ppm split into two different signals at δ 126.1 and 127.1 ppm. The ratio between the three signals at δ 126.1, 127.1, and 139.2 ppm was 1:2:1. At −60 °C the signals further separated to give new chemical shifts at δ 125.4, 127.4, and 139.4 ppm. The ratio between these signals was 4:13:1. We propose that the signal at δ 127.4 ppm (−60 °C) corresponds to the $Pd[P(OPh)_3]_4$ complex. At higher temperatures, this complex is in an equilibrium with $Pd[P(OPh)_3]_3$ and $P(OPh)_3$, giving rise to a broadened signal. At low temperatures, the tetracoordinated complex is more stable than the $Pd[P(OPh)_3]_3$ complex.

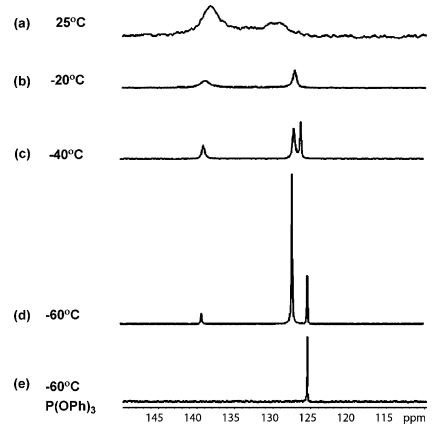

Figure 2. VT-$^{31}P\{^1H\}$ NMR spectra (121 MHz) performed in 0.6 mL of C_7D_8 $Pd(dba)_2$ (15 mM) + $P(OPh)_3$ (60 mM) with H_3PO_4 as an external standard at temperatures between 25 and −60 °C.

$Pd(dba)[P(OPh)_3]_2$ was prepared by addition of 2 equiv of $P(OPh)_3$ to $Pd(dba)_2$ in dry, degassed CH_2Cl_2 at room temperature under argon. The complex was purified by inert column chromatography and recrystallized from a saturated solution of pentane/CH_2Cl_2 at −20 °C, affording yellowish-green X-ray-quality single crystals in a 74% yield. The compound was air sensitive and decomposed after a few seconds in air and also in solution under inert conditions. The formulation of $Pd(dba)[P(OPh)_3]_2$ was confirmed by single-crystal X-ray crystallography. The molecular structure of the complex is shown in Figure 3. The central Pd(0) atom is coordinated in a trigonal planar way with respect to the two phosphorus atoms and the center of the two carbon atoms (η^2-coordination). The corresponding angles are P−Pd−P 105.1(2)° and P−Pd−C 102.7(5)° and 115.4(5)°. The arrangement has small deviations of the atoms from the

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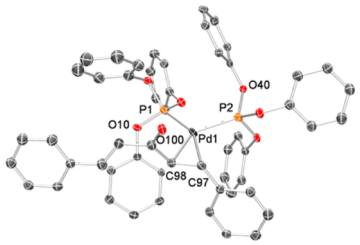

Figure 3. ORTEP representation of Pd(dba)[P(OPh)$_3$]$_2$ at thermal ellipsoids of 50%. Hydrogen atoms and CH_2Cl_2 solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Pd1−C97 2.126(15), Pd1−C98 2.159(15), Pd1−P1 2.247(5), Pd1−P2 2.254(5), C97−C98 1.348(19), C97−Pd1−C98 36.7(5), P1−Pd1−P2 105.14(17), C97−Pd1−P2 102.7(5), C98−Pd1−P1 115.4(5).

least-squares (l.s.) plane (0.05 Å rms). The Pd−P bond distances are in the range 2.244(5)−2.251(5) Å, which is considerably shorter than in analogous palladium phosphine complexes (2.277−2.348 Å)[15] and similar to an example of a dinuclear palladium bistriphenylphosphite complex (2.251−2.271 Å) in accordance with the π-acidity of the triphenylphosphite ligand.[16] The P−O distances are 1.585(4)−1.621(4) Å. The P(OPh)$_3$ units are arranged in a paddle wheel structure. The bond distance of the coordinated olefin (C97═C98 of 1.348(19) Å) is similar to the free olefin (C101═C102 of 1.329(18) Å) but significantly shorter than in the related Pd(dba)[PPh$_3$]$_2$ (C═C of 1.395(7) Å).[17] As expected, the two phosphorus atoms of Pd(dba)[P(OPh)$_3$]$_2$ are crystallographically nonequivalent (Figure 3); thus the ^{31}P NMR spectrum exhibits two broad signals for the complex (Figure 1).

Pd[P(OPh)$_3$]$_3$ was prepared in accordance with a literature procedure.[6c] Recrystallization of the complex from cold acetone afforded white X-ray-quality single crystals in 55% yield. The solid-state structure of Pd[P(OPh)$_3$]$_3$ was confirmed by a single-crystal X-ray crystallographic study. The molecular structure of the complex is shown in Figure 4. The central

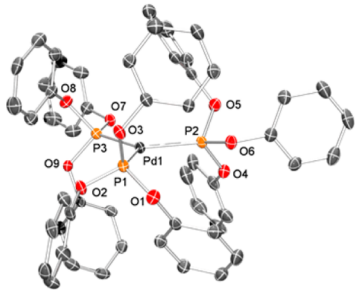

Figure 4. ORTEP representation of Pd[P(OPh)$_3$]$_3$ at thermal ellipsoids of 50%. Only one of the two independent units is displayed. Hydrogen atoms and acetone solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [deg]: P1−Pd1 2.2498(14), P2−Pd1 2.2525(14), P3−Pd1 2.2573(14), P1−Pd1−P2 116.03(5), P1−Pd1−P3 120.93(5), P2−Pd1−P3 122.94(5).

Pd(0) atom is coordinated in a trigonal planar fashion with only small deviations of the atoms from the l.s. plane (0.001 Å for Pd). The Pd−P bond distances are in the range 2.2431(3)−2.2572(3) Å, which is considerably shorter than in analogous palladium phosphine complexes[15] and similar to an example of a dinuclear palladium bistriphenylphosphite complex in accordance with the π-acidity of the triphenylphosphite ligand.[16] The P−O distances are 1.6087(2)−1.6373(2) Å and hence very similar to the free ligand. The P(OPh)$_3$ units are arranged in a paddle wheel structure. As expected, the three phosphorus atoms of Pd[P(OPh)$_3$]$_3$ are identical and imply a high molecular symmetry (Figure 4); thus the ^{31}P NMR spectrum exhibits one signal for the complex (Figure 1) The steric hindrance by the bulkier triphenylphosphite ligand may explain why three and not four ligands are the preferred coordination to the metal as compared to PPh$_3$.

The two pure complexes were evaluated in the allylation of aniline by allyl alcohol under identical reaction conditions (Figure 5). The measurements of the catalytic activity of pure

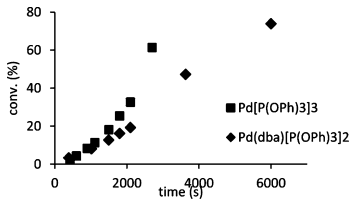

Figure 5. Pd(dba)[P(OPh)$_3$]$_2$ and Pd[P(OPh)$_3$]$_3$ complexes in the allylation of aniline by allyl alcohol. Reaction conditions: allyl alcohol (0.840 M), aniline (0.209 M), Pd catalyst (2 mol %), C_6D_6, 60 °C.

Pd(dba)[P(OPh)$_3$]$_2$ and Pd[P(OPh)$_3$]$_3$ showed that the Pd(dba)[P(OPh)$_3$]$_2$ complex exhibited a 70% lower reactivity than the Pd[P(OPh)$_3$]$_3$ complex. This may suggest that a fast equilibrium of the Pd(dba)[P(OPh)$_3$]$_2$ complex and Pd[P(OPh)$_3$]$_3$ was operating. In fact, this would correspond to the equilibrium study where the observed ratio of Pd(dba)[P(OPh)$_3$]$_2$ and Pd[P(OPh)$_3$]$_3$ was 1:3 at a Pd(dba)$_2$:P(OPh)$_3$ ratio of 1:2 (*vide supra*, Figure 1d). Thereby, the reactivity of Pd(dba)[P(OPh)$_3$]$_2$ (70% of the reactivity for pure Pd[P(OPh)$_3$]$_3$) was within experimental error of what was expected for the actual concentration of Pd[P(OPh)$_3$]$_3$ (75%) at a Pd(dba)$_2$:P(OPh)$_3$ ratio of 1:2. It should be noted that the pure complex and the *in situ* prepared complex showed equal reactivity. Furthermore, excess triphenylphosphite ligand (16 equiv) did not inhibit the reactivity as compared to the DBP ligand.[10]

ESI-MS monitoring of the palladium-catalyzed allylic substitution of allyl alcohol (Figures 6 and 7) was used to

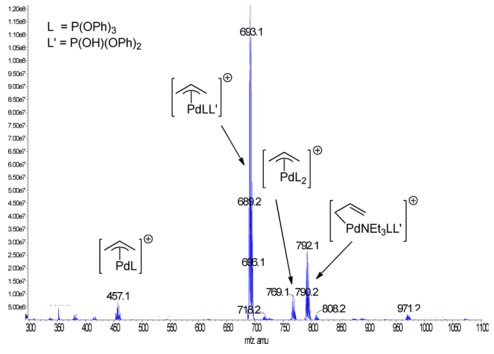

Figure 6. ESI mass spectrum of reaction of Pd(dba)[P(OPh)$_3$]$_2$ + allyl alcohol after 5 min at 60 °C.

determine whether Pd[P(OPh)$_3$]$_3$ and Pd(dba)[P(OPh)$_3$]$_2$ generated the same reactive catalyst.[13,18] Samples were withdrawn from the reaction mixture of either Pd(dba)-[P(OPh)$_3$]$_2$ or Pd[P(OPh)$_3$]$_3$ together with allyl alcohol after 5 min reaction time. The ESI(+)-MS spectrum shows the same

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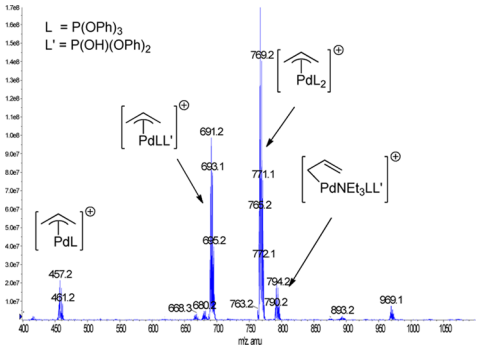

Figure 7. ESI mass spectrum of reaction of $Pd[P(OPh)_3]_3$ + allyl alcohol after 5 min at 60 °C.

signals that correspond to π-allylpalladium intermediates for both catalyst precursors but at different intensities (all m/z values are given for the most abundant ^{106}Pd complex). These species were characterized by collision-induced dissociation via ESI(+)-MS/MS experiments (SI). The identical ESI-MS patterns (SI) of allylic substitution with both $Pd(dba)[P(OPh)_3]_2$ (Figure 6) and $Pd[P(OPh)_3]_3$ (Figure 7) indicate that $Pd[P(OPh)_3]_2$ is generated from $Pd(dba)[P(OPh)_3]_2$ by loss of dba to generate $Pd[P(OPh)_3]_2$ as the active species for the allylation reaction. Interestingly, the reaction mixture initially containing $Pd[P(OPh)_3]_3$ gives higher intensities of the active π-allyl-$Pd[P(OPh)_3]_2$ complex and less of the decomposed π-allyl-$PdP(OPh)_3P(OH)(OPh)_2$ complex compared to the reaction mixture initially containing $Pd(dba)[P(OPh)_3]_2$, and this may reflect their relative stabilities in solution.

In conclusion we have isolated pure $Pd(dba)[P(OPh)_3]_2$ and $Pd[P(OPh)_3]_3$ complexes. The equilibrium between $Pd(dba)_2$ and $P(OPh)_3$ has been studied. $Pd[P(OPh)_3]_3$ is the favored complex in solution at room temperature. At lower temperatures, the $Pd[P(OPh)_3]_4$ is the favored complex. Both $Pd(dba)[P(OPh)_3]_2$ and $Pd[P(OPh)_3]_3$ complexes generate $Pd[P(OPh)_3]_2$, which is the active species in catalysis; however $Pd[P(OPh)_3]_3$ is more stable.

EXPERIMENTAL SECTION

Preparation of $Pd(dba)[P(OPh)_3]_2$. A flame-dried Schlenk tube was charged with $Pd(dba)_2$ (40 mg, 0.0696 mmol), dissolved in 0.4 mL of CH_2Cl_2, and $P(OPh)_3$ (36 μL, 0.139 mmol) was added via syringe. The slurry was degassed by three freeze–pump–thaw cycles and stirred at room temperature for 30 min. The solvent was removed *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel using argon-bubbled solvents. The first band, yellow, was eluted with CH_2Cl_2 to remove free dba ligand. The second band, green, containing the complex, was eluted with Et_2O. The solution was frozen and the solvent was removed *in vacuo* to afford $Pd(dba)[P(OPh)_3]_2$ (49 mg, 74% yield) as a green solid. The complex was recrystallized from a saturated solution of pentane/CH_2Cl_2 at −20 °C, affording yellowish-green air-sensitive crystals. ^1H NMR (500 MHz, C_6D_6): δ 7.89–7.71 (brd, 2H), 7.29–7.19 (brs, 4H), 7.11–6.97 (m, 30H), 6.95–6.75 (m, 8H). ^{13}C NMR (126 MHz, C_6D_6): It was impossible to characterize by ^{13}C NMR due to its rapid decomposition in solution and also rapid transformation to $Pd[P(OPh)_3]_3$. The complex requires handling under an inert atmosphere at low temperature. $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ 137.6, 133.4. IR (Nujol, cm^{-1}): 3059, 2923, 2853, 1649, 1591, 1481, 1442, 1333, 1190, 1160, 1087, 1071, 1024, 978, 899, 873, 776, 688. MS (ESI-TOF): calcd for $[C_{53}H_{45}O_7P_2Pd]^+$ 961.1675, found 961.1688 ($M + H^+$).

ASSOCIATED CONTENT

Supporting Information

Full experimental section, including characterization of compounds as well as CIF files giving X-ray data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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