A New Type of Chainlike Tetranuclear Rhodium Complexes with PR_3 and $AsMe_3$ as Bridging Ligands**

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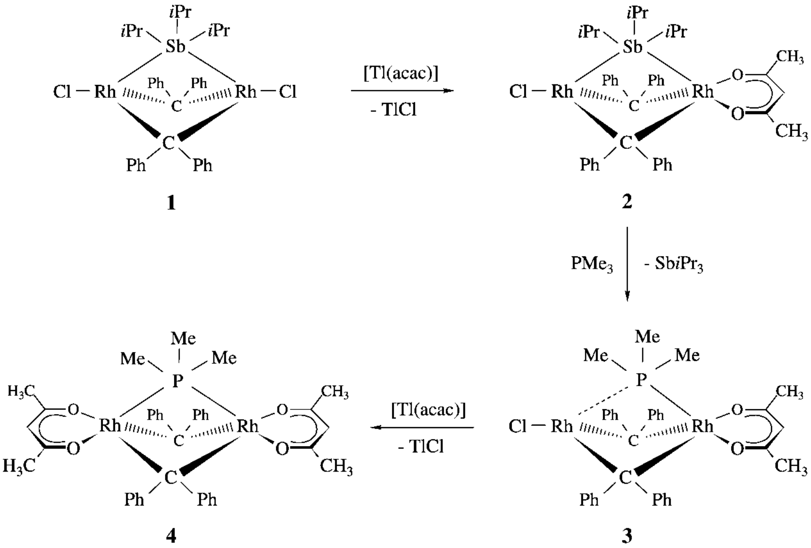
Dedicated to Professor Wolfgang Beck on the occasion of his 70th birthday

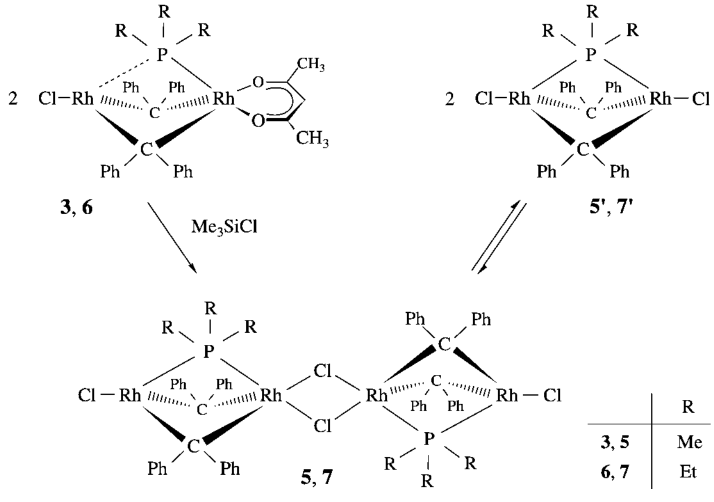
In the context of our studies on the reactivity of square-planar carbenerhodium(I) compounds *trans*-$[RhCl(=CRR')(L)_2]$ with $L = PR_3$, AsR_3, SbR_3,[1] we previously observed that the bis(stibane) derivatives *trans*-$[RhCl(=CRR')(Sb\mathit{i}Pr_3)_2]$ generate upon heating dinuclear rhodium(I) complexes with $[Rh(\mu\text{-}Sb\mathit{i}Pr_3)Rh]$ as a building block.[2] After initial attempts to substitute the triisopropylstibane in **1** by a tertiary phosphane or arsane failed,[2] we circumvented the difficulties by the sequence of reactions shown in Scheme 1. The crucial observation was that replacing one of the chloro ligands in **1** by acetylacetonate (acac) changes the reactivity of the starting material significantly and provides the opportunity to substitute $Sb\mathit{i}Pr_3$ for PMe_3 without fragmentation of the dinuclear molecular core. Subsequent reaction of **3** with [Tl(acac)] affords the symmetrical bis(acac) complex **4** in virtually quantitative yield.[3]



Scheme 1. Indirect substitution of the $Sb\mathit{i}Pr_3$ ligands in **1** by PMe_3 and subsequent reaction to give **4**.

While both the NMR spectra and the X-ray structure analysis of **3** clearly indicate that the phosphane ligand is in a "semibridging" position,[3, 4] the data for **4** are somewhat different. The ^{31}P NMR spectrum of **4** displays a sharp triplet (due to $^{31}P-^{103}Rh$ coupling) which does not broaden or split into a doublet of doublets upon cooling the solution in $[D_8]$toluene at −80 °C. However, the two Rh–P bond lengths (2.2707(7) and 2.5700(8) Å) are not exactly the same, which we explained, taking the NMR data into consideration, by packing effects in the lattice.[3]

To find out how strongly the *anionic* ligands influence the binding of the bridging moieties to the metal centers, we studied a variety of substitution reactions of the phosphane-bridged compounds **3** and **4** of which those with Me_3SiCl furnished a breakthrough (Scheme 2). Treatment of **3** with an excess of the chlorosilane in benzene led to a smooth replacement of acac by chloride and gave a red solid **5**, which correctly analyzed as $[Rh_2Cl_2(CPh_2)_2(PMe_3)]$, in 92 % yield. The reaction of **6**[3] with Me_3SiCl in the molar ratio of about 1:200 proceeded analogously and gave the PEt_3-bridged species **7** in 85 % yield. While we anticipated, owing to the ^1H and ^{13}C NMR spectra of **5** and **7**, that both compounds would possess a structure analogous to that of the stibane-bridged complex **1**, the X-ray crystal structure analysis of **5** revealed that in the lattice two dinuclear moieties are connected through two bridging chloro ligands to give a Rh_4 species with a chainlike $\{ClRh_2Cl_2Rh_2Cl\}$ core (Figure 1).[5] Moreover, the midpoint of the planar $Rh(\mu\text{-}Cl)_2Rh$ fragment is a center of symmetry. Besides the Rh1–Rh2 distance of 2.5054(2) Å, which differs only slightly to that of the stibane-bridged compound **1** (2.5349(5) Å),[2] the most important structural features of **5** are the Rh–P bond lengths of 2.3625(6) Å and 2.4826(6) Å. The difference between these two distances is much less than for the bis(acac) complex **4** indicating that—at least in the crystal lattice—the type of the anionic ligands bonded to the rhodium center influences the position of the bridging phosphane unit. Owing to the similarity of the Rh–Rh and Rh–P distances, the bond angles of the Rh_2P triangle are nearly the same and deviate only marginally from the 60° value.



Scheme 2. Synthesis of the tetranuclear rhodium complexes **5** and **7**, which are in equilibrium with the dinuclear complexes **5′** and **7′**.

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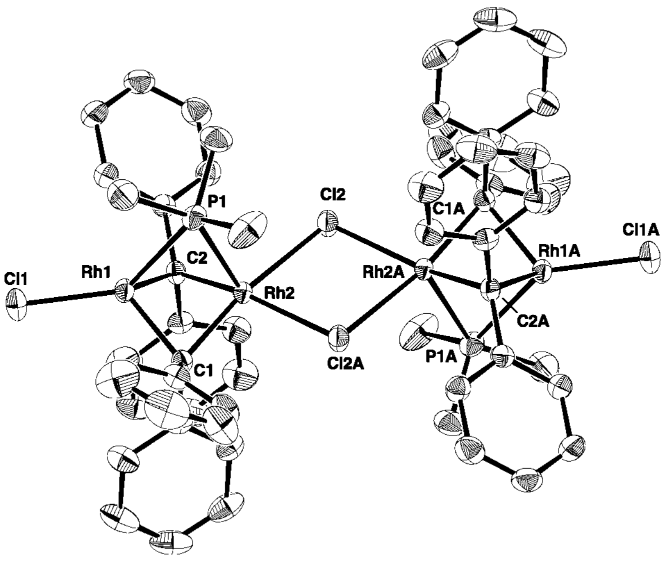


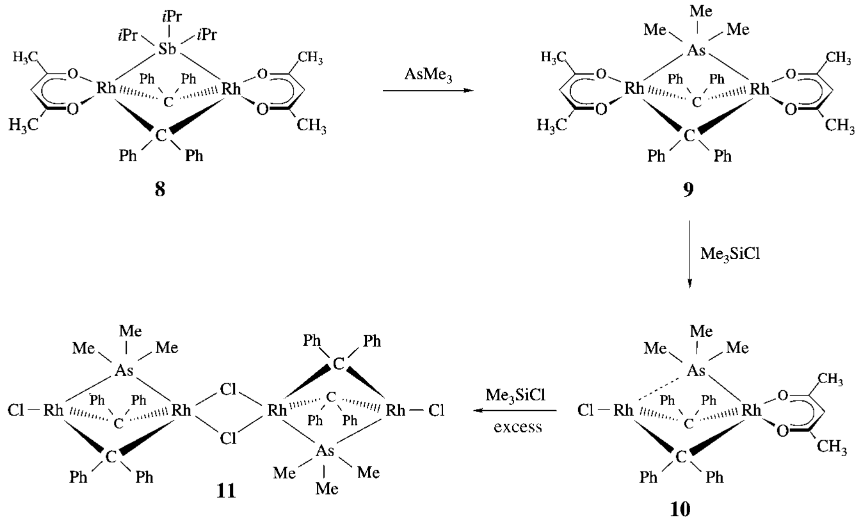
Figure 1. Molecular structure of **5** in the crystal. Selected bond lengths [Å] and angles [°]: Rh1-Rh2 2.5054(2), Rh1-P1 2.4826(6), Rh2-P1 2.3625(6), Rh1-C1 1.988(2), Rh1-C2 1.968(2), Rh2-C1 2.044(2), Rh2-C2 2.051(2), Rh1-Cl1 2.3088(6), Rh2-Cl2 2.4961(5); Cl1-Rh1-Rh2 167.894(19), Cl1-Rh1-P1 135.51(2), Cl1-Rh1-C1 122.43(6), Cl1-Rh1-C2 119.98(6), Rh1-C1-Rh2 76.83(7), Rh1-C2-Rh2 77.08(7), Rh1-P1-Rh2 62.217(15), C1-Rh1-C2 91.09(8), C1-Rh2-C2 87.19(8), C1-Rh1-P1 87.06(6), C2-Rh1-P1 88.43(6), C1-Rh2-P1 89.11(6), C2-Rh2-P1 89.88(6), Rh1-Rh2-Cl2 137.252(14), C1-Rh2-Cl2 170.77(6), C2-Rh2-Cl2 96.33(6), P1-Rh2-Cl2 99.41(2).

Although cryoscopic measurements with a saturated solution of **5** in benzene confirm that under these conditions the tetranuclear compound is present (calcd: $M_r = 1370.4$; found: $M_r = 1310$), the ^{31}P NMR spectrum of **5** at room temperature (in C_6D_6) is concentration-dependent. The spectrum of a nearly saturated solution (4 mmolL^{-1}) exhibits a somewhat broadened triplet at $\delta = -24.6$ ppm which after lowering the concentration to 0.1 mmolL^{-1} transforms into a sharp triplet with a chemical shift of $\delta = -20.4$ ppm. Since the data in CD_2Cl_2 are quite similar (a broadened triplet being observed at $\delta = -23.1$ ppm for a concentrated and a sharp triplet at $\delta = -15.7$ ppm for a diluted solution), we conclude that both in benzene and dichloromethane a rapid equilibrium between the Rh_4 and the Rh_2 species exists (see Scheme 2), and that at low concentrations the Rh_2 species **5'** dominates. At −80 °C in [D_8]toluene, the ^{31}P NMR spectrum of **5** displays a doublet of doublets at $\delta = -30.4$ (with $^{31}P-^{103}Rh$ coupling constants of 128.4 and 95.4 Hz) indicating that under these conditions the conversion of **5** to **5'** is inhibited.

After attempts to generate a dinuclear rhodium(I) complex with a trialkylarsane as a bridging ligand by treatment of the stibane derivative **1** with $AsMe_3$ or $As\textit{i}Pr_3$ failed, we succeeded in preparing the "missing link" between the [Rh(μ-SbR_3)Rh] and [Rh(μ-PR_3)Rh] compounds in a stepwise manner. Whereas the reaction of **8**[6] even with a large excess of $AsMe_3$ in benzene leads to a equilibrium mixture of **8** and **9**, in hexane as solvent (in which **9** is only sparingly soluble) the arsane-bridged complex **9** is obtained (6 h, 25 °C) as a light-brown solid in 85 % yield (Scheme 3). Although **9** can be stored under argon at −25 °C for weeks, in solution (benzene or acetone) it decomposes quite rapidly.

Despite its lability, compound **9** reacts with Me_3SiCl (molar ratio 1:1.1) to give the dinuclear complex **10**, which possibly contains the arsane in a semibridging coordination mode. As already observed with the PMe_3 counterparts **3** and **4**, the unsymmetrical species **10** is significantly more stable than **9** and does not decompose in benzene even after storing for three days. Replacing the remaining acac ligand of **10** by chloride is more difficult and, even with a large excess of Me_3SiCl, the formation of **11** occurs only slowly at room temperature. After removal of the volatiles, the dichloro derivative was isolated as a red-brown solid in 91 % yield. As shown by the X-ray crystal structure analysis,[5] the symmetrical $AsMe_3$-bridged compound **11** is isomorphous to **5** and also possesses the midpoint of the Rh(μ-Cl)$_2$Rh unit as a center of symmetry (Figure 2). For both **5** and **11**, each half-dimer structure is found twice in the asymmetric unit. However, the most noteworthy structural feature of **11** is that in contrast to **5** the terminal Cl−Rh bond length is longer than the Cl−Rh distances in the bridge. For this observation there is no precedence. The two Rh−As bond lengths of **11** differ slightly (2.5475(4) and 2.6731(4) Å) reflecting the inequivalence of the "outer" and "inner" metal centers of the {$ClRh_2Cl_2Rh_2Cl$} chain. Since the ^1H as well as the ^{13}C NMR spectra of **11** (in CD_2Cl_2) remain unchanged in the temperature range between 193 K and 333 K, we assume that under these conditions no dissociation of the dimeric Rh_4 to the monomeric Rh_2 species takes place.

The results of the present investigation close a gap in the field of coordination chemistry. After it had been supposed for decades that tertiary phosphanes, arsanes, and stibanes behave exclusively as terminal ligands, it was only recently that this postulate became weakened. The preparation of compound **1** (the first "outsider")[7] and its $SbMe_3$ and $SbEt_3$ analogues[2] was followed by the isolation and structural characterization of **3** and **4** and has now culminated in the



Scheme 3. Substitution of the Sb$\textit{i}$Pr$_3$ ligands in **8** by $AsMe_3$ and subsequent reaction to give **11**.

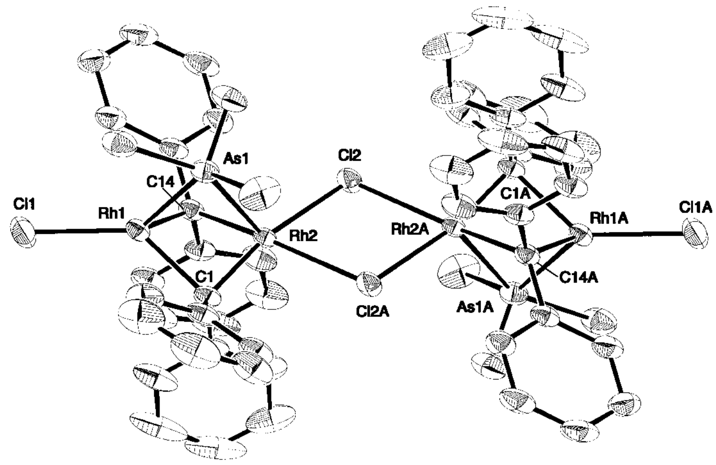


Figure 2. Molecular structure of **11** in the crystal. Selected bond lengths [Å] and angles [°]: Rh1-Rh2 2.8407(3), Rh1-As1 2.5475(4), Rh2-As1 2.6731(4), Rh1-C1 2.129(3), Rh1-C14 1.934(3), Rh2-C1 1.862(3), Rh2-C14 2.157(3), Rh1-Cl1 2.5589(8), Rh2-Cl2 2.3667(7); Cl1-Rh1-Rh2 171.03(2), Cl1-Rh1-As1 129.62(2), Cl1-Rh1-C1 136.21(7), Cl1-Rh1-C14 124.40(8), Rh1-C1-Rh2 90.53(10), Rh1-C14-Rh2 87.78(10), Rh1-As1-Rh2 65.881(10), C1-Rh1-C14 77.91(10), C1-Rh2-C14 78.73(10), C1-Rh1-As1 80.97(7), C14-Rh1-As1 90.24(8), C1-Rh2-As1 82.53(9), C14-Rh2-As1 82.40(7), Rh1-Rh2-Cl2 141.653(18), C1-Rh2-Cl2 168.26(9), C14-Rh2-Cl2 196.61(7), As1-Rh2-Cl2 108.32(2).

synthesis of the first arsane-bridged species **9**–**11**. As Braunstein and Boag pointed out last year,[8] a bonding mode such as {M(μ-ER$_3$)M} (E = P, As, Sb) should not be regarded as thermodynamically unfavorable and, taking both the isolobal analogy of SiR$_3^-$ and PR$_3$ and the existence of silyl-bridged transition-metal complexes into consideration,[8] the preparation of **1**, **4**, **5**, **9**, and **11** might only be the first step into a new field. The recent discovery by Reau and Halet et al.[9] that the phosphorus atom of substituted phospholes is able to bridge two palladium centers undoubtedly supports this prediction.

Experimental Section

5: A solution of **3** (518 mg, 0.69 mmol) in benzene (70 mL) was treated with Me$_3$SiCl (1 mL, 7.9 mmol) and stirred for 24 h at room temperature. The solvent and excess silane were evaporated in vacuo, the red solid was washed with diethyl ether (2 × 5 mL) and dried: yield 436 mg (92 %); m.p. 126 °C (decomp); ^{1}H NMR (400 MHz, C$_6$D$_6$, 4 mmol L^{-1}, 293 K):[10] δ = 0.88 ppm (d, ^2J(P,H) = 10.6 Hz; PCH$_3$); ^{13}C NMR (100.6 MHz, C$_6$D$_6$, 4 mmol L^{-1}, 293 K): δ = 187.8 (m; *C*Ph$_2$), 23.5 ppm (d, ^1J(P,C) = 40.0 Hz; PCH$_3$); ^{31}P NMR (81.0 MHz, C$_6$D$_6$, 4 mmol L^{-1}, 293 K): δ = −24.6 ppm (br t, ^1J(Rh,P) = 109.4 Hz); ^{31}P NMR (81.0 MHz, C$_6$D$_6$, 0.1 mmol L^{-1}, 293 K): δ = −20.4 ppm (t, ^1J(Rh,P) = 109.3 Hz); ^{31}P NMR (81.0 MHz, [D$_8$]toluene, 2 mmol L^{-1}, 293 K): δ = −21.3 ppm (t, ^1J(Rh,P) = 111.9 Hz); ^{31}P NMR (81.0 MHz, [D$_8$]toluene, 2 mmol L^{-1}, 193 K): δ = −30.4 ppm (dd, ^1J(Rh,P) = 128.4 and 95.4 Hz).

Compound **7** was prepared as described for **5**, by using **6** (132 mg, 0.17 mmol) and Me$_3$SiCl (5 mL, 39.4 mmol) as starting materials. Red solid: yield 103 mg (85 %); m.p. 85 °C (decomp); ^{1}H NMR (400 MHz, C$_6$D$_6$):[10] δ = 0.77 ppm (m; PC*H*$_2$C*H*$_3$); ^{13}C NMR (100.6 MHz, C$_6$D$_6$): δ = 186.7 (m; *C*Ph$_2$), 22.0 (d, ^1J(P,C) = 34.3 Hz; PCH$_2$), 9.3 ppm (d, ^2J(P,C) = 4.8 Hz; PCH$_2$*C*H$_3$); ^{31}P NMR (162.0 MHz, C$_6$D$_6$, 293 K): δ = 4.8 ppm (t, ^1J(Rh,P) = 102.5 Hz).

Compound **9** was prepared from **8** (553 mg, 0.56 mmol) and AsMe$_3$ (108 µL, 1.0 mmol). Light brown solid: yield 408 mg (85 %); m.p. 105 °C (decomp); ^{1}H NMR (200 MHz, C$_6$D$_6$, 293 K):[10] δ = 5.50 (s; CH of acac), 1.95 (s; CH$_3$ of acac), 0.88 ppm (s; AsCH$_3$); ^{13}C NMR (100.6 MHz, CD$_2$Cl$_2$, 233 K): δ = 188.0 (s; CO of acac), 172.7 (t, ^1J(Rh,C) = 22.4 Hz; *C*Ph$_2$), 99.5 (s; CH of acac), 27.8 (s; CH$_3$ of acac), 18.0 ppm (s; AsCH$_3$). Compound **10** was prepared analogously as described for **5**, by using **9** (76 mg, 0.09 mmol) and Me$_3$SiCl (12 µL, 0.10 mmol) as starting materials; reaction time 1 h. Brown solid: yield 62 mg (88 %); m.p. 105 °C (decomp); ^{1}H NMR (400 MHz, C$_6$D$_6$, 293 K):[10] δ = 5.41 (s; CH of acac), 1.89 (s; CH$_3$ of acac), 0.62 ppm (s; AsCH$_3$); ^{13}C NMR (100.6 MHz, C$_6$D$_6$): δ = 189.1 (s; CO of acac), 178.2 (dd, ^1J(Rh,C) = 27.2 and 20.0 Hz; *C*Ph$_2$), 101.0 (s; CH of acac), 28.0 (s; CH$_3$ of acac), 18.6 ppm (s; AsCH$_3$).

Compound **11** was prepared from **10** (75 mg, 0.09 mmol) and excess Me$_3$SiCl (2 mL, 15.7 mmol) in benzene (2 mL). Red-brown solid: yield 63 mg (91 %); m.p. 120 °C (decomp); ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 293 K):[10] δ = 1.19 ppm (s; AsCH$_3$); ^{13}C NMR (100.6 MHz, CD$_2$Cl$_2$, 293 K): δ = 20.5 ppm (s; AsCH$_3$).

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[5] Data for the X-ray structure analyses: **5**: Crystals from benzene, C$_{58}$H$_{58}$Cl$_4$P$_2$Rh$_4$ · 2 C$_6$H$_6$ (M_r = 1526.64); crystal size 0.4 × 0.4 × 0.2 mm^3; monoclinic, space group $P2_1/c$ (no. 14), a = 22.2854(11), b = 15.1150(7), c = 19.2895(9) Å, β = 101.8780(10)°, Z = 4, V = 6358.4(5) Å^3, ρ_{calcd} = 1.595 g cm^{-3}; T = 173(2) K; 2θ = 50.00°; 60158 reflections measured, 11183 were unique (R_{int} = 0.0228), and 10525 observed ($I > 2\sigma(I)$); Bruker Smart Apex diffractometer with D8 goniometer equipped with a low-temperature device in ω mode,[11] Mo$_{K\alpha}$ radiation (λ = 0.71073 Å), graphite-monochromated; Lp correction. The structure was solved by the Patterson method and refined with the full-matrix, least-squares method; R_1 = 0.0228, wR_2 = 0.0541 (for 10525 reflections with $I > 2\sigma(I)$, R_1 = 0.0249, wR_2 = 0.0551 (for all 11183 data); data-to-parameter ratio 15.38; residual electron density +0.472/−0.351 e Å^{-3}. **11**: Crystals from benzene, C$_{58}$H$_{58}$As$_2$Cl$_4$Rh$_4$ · 2 C$_6$H$_6$ (M_r = 1614.55); crystal size 0.67 × 0.66 × 0.63 mm^3; monoclinic, space group $P2_1/c$ (no. 14), a = 19.4838(11), b = 15.2521(9), c = 22.4012(13) Å, β = 102.5350(10)°, Z = 4, V = 6498.3(7) Å^3, ρ_{calcd} = 1.650 g cm^{-3}; T = 173(2) K; 2θ = 49.42°; 73301 reflections measured, 10944 were unique (R_{int} = 0.0208), and 10117 observed ($I > 2\sigma(I)$); Bruker Smart Apex diffractometer with D8 goniometer equipped with a low-temperature device in ω mode,[11] Mo$_{K\alpha}$ radiation (λ = 0.71073 Å), graphite-monochromated; Lp correction. The structure was solved by direct methods and refined with the full-matrix, least-squares method; R_1 = 0.0274, wR_2 = 0.0719 (for 10117 reflections with $I > 2\sigma(I)$, R_1 = 0.0300, wR_2 = 0.0734 (for all 10944 data); data-to-parameter ratio 15.05; residual electron density +0.919/−0.593 e Å^{-3}. CCDC-178267 (**5**) and CCDC-178268 (**11**) contain the supplementary crystallographic data for this paper. These data 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) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[10] The ^{1}H and ^{13}C NMR data of the phenyl groups were omitted for simplicity.

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