Palladium(II) Complexes Containing P~N~O Donors. Preparation and Reactivity

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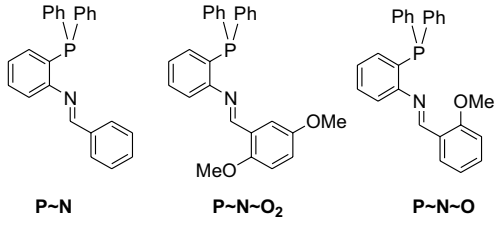
Palladium complexes [(**P~N~O**)PdR]BF_4 containing imine-phosphine-ether tridentate donor were prepared. The behavior of an ether donor, a hemi-labile one, influences the coordination mode of a carbon ligand around the metal center. Reaction of excess styrene with [(**P~N~O**)PdMe]BF_4 results in the formation of [(**P~N~O**)Pd(η^3-CH(CH_3)C_6H_5)]BF_4, which is characterized by spectral and crystal structural determination. Copolymerization of olefin and carbon monoxide catalyzed by [(**P~N~O**)PdMe]BF_4 is addressed.

Keywords: Imine-phosphine; Tridentate; Palladium; Polymerization.

INTRODUCTION

Considerable research on development of palladium complexes bearing bidentates as catalysts for polymerization or copolymerization of olefins and/or carbon monoxide provide us fruitful information on understanding such reactions.[1] It appears that ligand design for better catalytic activity particularly in polymerization continues to be an interesting area of research.[2] Among them, metal complexes with bulky ligand environment have been found to be catalytically active in polymerization of ethylene with high molecular weight.[1] However, effects on the hemi-labile donor within multidentate ligands on metal-catalyzed polymerization is less addressed.[3-5] Recently, we found that the cationic palladium complex [(**P~N**)PdMeL]$^+$ is a good catalyst for di- and trimerization of ethylene, but not polymerization.[6f] However, the introduction of a labile donor into a **P~N** system makes the complex of [(**P~N~O$_2$**)PdMe]$^+$ be a catalyst for oligomerization of ethylene.[6e] Continuing this trend, we report here the effect of a hemi-labile donor on the migratory insertion of olefin and carbon monoxide into a Pd-C bond of [(**P~N~O**)PdMe]BF_4.



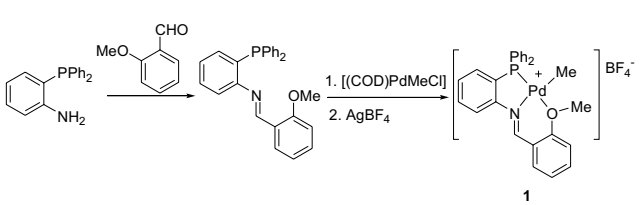
P~N **P~N~O$_2$** **P~N~O**

RESULTS AND DISCUSSION

Synthesis of Palladium(II) Complex

Tridentate **P~N~O** ligand was prepared by the condensation of *o*-(diphenylphosphino)aniline with *o*-methoxybenzaldehyde under acidic conditions (Scheme I). Characteristic spectral data of infrared absorption at 1628 cm^{-1} and ^{13}C NMR shift at 159.6 ppm confirm the formation of imine functionality. Substitution reaction of [(COD)PdMeCl] with **P~N~O** followed by the treatment of silver tetrafluoroborate gives the cationic **P~N~O** tridentate palladium complex **1** as yellow solids in good isolated yield. The ^{31}P NMR spectrum of the complex displays a singlet at δ 42.0, which is in agreement with the reported species [(**P~N**)PdMe(CH_3CN)]BF_4 (δ 38.6). A doublet signal at δ 0.6 ($J_{P\text{-}H}$ = 0.6 Hz) in the ^1H NMR spectrum is the typical chemical shift for Pd-CH_3, and splitting caused by the phosphorus-31 also confirms the coordination of phosphine toward the metal center. Coordination of the methoxy group is also verified by both ^1H and ^{13}C NMR coordination shifts. The bound methoxy displays a signal at δ

Scheme I Preparation of Palladium Complex **1**



1

Dedicated to Professor Fa-Ching Chen on the occasion of his ninetieth birthday.

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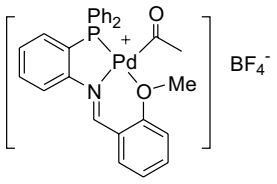
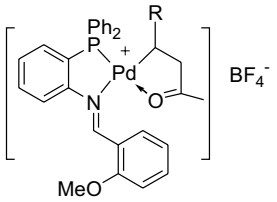
4.25 ppm, which is down-field shifted from δ 3.85 of the free ligand, whereas the ^{13}C shift also appears with the same trend from δ 55.2 to 59.4. These spectral data clearly illustrate the complexation of an ether donor with palladium ion.

Insertion of Carbon Monoxide and Olefins

Carbonylation of **1** was carried out by a solution of **1** in dichloromethane and acetonitrile under carbon monoxide atmosphere (150 psi) to yield the palladium acetyl complex **2** in 75% isolated yield. It appears that the pressure and completion for carbonylation of **1** to yield **2** is much more severe than that for [(**P~N**)PdMe(CH_3CN)]BF_4 (**3**) indicating that the intramolecular coordination of ether does slow down the insertion process. Characterization of the inserted product was based on the spectroscopic and elemental analyses. Similar to complex **1**, the coordination chemical shift of ether also proves its chelation toward the metal center. Such a chelation effect increases the stability of **2**, which is stable in solution under nitrogen atmosphere for several days.



2



3 R = H
4 R = Ph

Further insertion of ethylene and styrene into the acyl complex **2** provides the corresponding products **3** and **4**, respectively. Both complexes are stable, yellow solids and their structures were identified by spectral methods. Unlike the coordination of an ether donor in the acyl complexes **2**, the fourth coordination site of a palladium center in both **3** and **4** is replaced by the carbonyl functionality, i.e. the methoxy group in **3** and **4** appears to be free. The infrared absorptions at ca. 1635 cm^{-1} in both **3** and **4** are characteristic stretching frequencies for the coordinated carbonyls, whereas the chemical shifts of the methoxy group show at δ 3.92, which is similar to that for the free ligand (Table 1).

Simple reactions of **1** with an equal-molar amount of olefins resulted in the formation of various unidentified and decomposed products with palladium black. However, instead of polymerization, reaction of **1** with excess of styrene provided the single insertion product **5**, which was identified by both ^1H and ^{13}C NMR spectroscopy. Chemical shifts of methine proton [δ 6.22, dq, J_{HH} = 15.7, J_{PH} = 6.4 Hz] and carbon [δ 55.9, $J_{P\text{-}C}$ = 26 Hz], as well as the ortho arene hydrogens [δ 6.91, J_{HH} = 8.4 Hz; δ 6.74, J_{HH} = 7.6 Hz, J_{PH} = 7.5 Hz] are characteristic for palladium π-benzyl complex.[7] A signal for the methyl group (δ 1.87, J_{HH} = 6.4 Hz) coupled with the methine proton was observed, indicating the formation of palladium π-styenyl complex. Confirmation of the structure was achieved by X-ray single crystal analysis (Fig. 1). ORTEP plot of **5** clearly shows that its structure is a η^3-π-styenyl complex. This structure is not consistent with the one of direct insertion of styrene into Pd-Me, which is normally obtained from such insertion as illustrated by Brookhart and coworkers in the species of [(N~N)Pd(η^3-$CH(CH_3CH_2)C_6H_5$)]$^+$.[7]

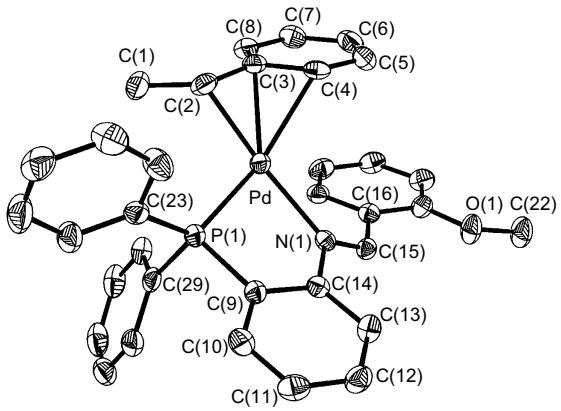


Fig. 1. ORTEP Plot of **5** (30% probability).

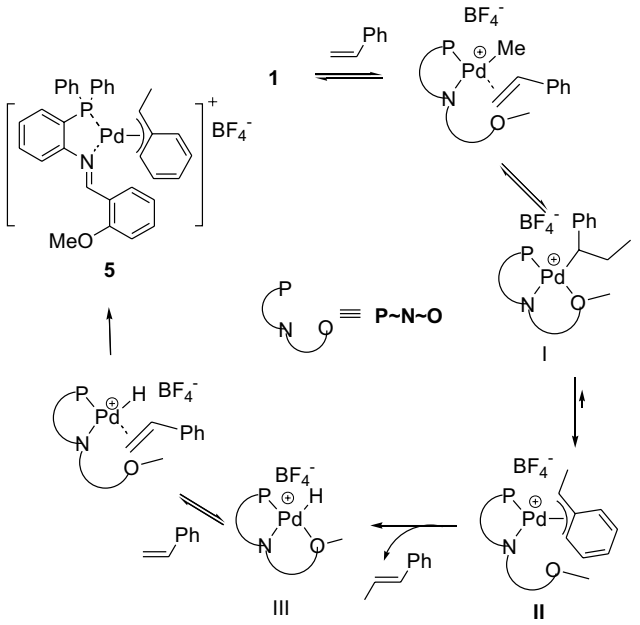
Table 1. Selected IR[a] and NMR[b] Absorptions of Free Ligand and Palladium Complexes

	Infrared		^1H NMR	Pd-***Me*** or	^{31}P NMR
	ν(C=N)	ν(C=O)	Ar-O***Me***	CO-***Me***	
P~N~O		-	3.85		-15.0
1	1602	-	4.25	0.60 (d, J = 0.6 Hz)	42.0
2	1621	1713	4.08	2.18	20.7
3	1602	1635	3.92	2.15	37.6
4	1602	1636	3.92	2.31	31.3
5	1612	-	3.84	-	31.1

[a] in KBr. cm^{-1}, [b] in $CDCl_3$

The possible reaction mechanism leading to **5** is demonstrated in Scheme II. Coordination of styrene followed by insertion to form **I** is the expected pathway for the migratory insertion of unsaturated substrate into Pd-Me. The β-elimination readily takes place to yield the Pd-H species **II** and propenylbenzene. The palladium hydride **II** was not observed by the ^{1}H NMR spectrum presumably due to its high activity. But the generation of propenylbenzene was detected in this NMR experiment, suggesting that it readily underwent subsequent insertion with another molecule of styrene to form the π-styenyl complex **5** at ambient temperature.

Scheme II Pathway of fomation π-allyl palladium complex **5**



Unlike the chelation effect on stabilization of Pd-acetyl complex **2**, the methoxy group in this ligand system does not persist in this kind of effect on the η^1-allyl intermediate **I**, indicating that the thermal stability of the coordination of η^3-π-styenyl is greater than that of **P~N~O** chelation. According to the measurement by Brookhart's group, the free energy change (ΔG°) for the conversion of [(**N~N**)Pd(η^3-CH(CH$_3$CH$_2$)C$_6$H$_5$)]$^+$ into [(**N~N**)Pd(η^3-CH(CH$_3$)C$_6$H$_5$)]$^+$ is -3.2 Kcal/mol,[7] indicating a favorable process for elimination of propenylbenzene, which is consistent with our results.

Crystallography

The ORTEP plots and the selected bond lengths as well as bond angles for **5** are shown in Fig. 1 and Table 2 respectively. The palladium metal was surrounded by donor atoms of phosphine (P1), imino-nitrogen (N1) and η^3-π-styenyl with the π-bonding of benzene ring seated *trans* to the phosphorus. The π-bonding modes have been observed in previous reactions involving the alkyne insertion into Pd-C bonds,[6d,8-10] as well as palladium diimine complexes reported by Brookhart and coworkers.[7] The bond lengths between the Pd and P, N donor atoms for **5** are within the range and comparable with the known species.[7] A large deviation was found in the bond angle of P1-Pd-N1 [82.60(9)°], which is similar to those of palladium complexes containing **P~N** in *o*-phenylene linkage.[6] As for the angle of C2-C3-C4 [116.6(4)°], it is slightly smaller than 120° presumably due to steric relief between a phenyl ring and π-styenyl ligands. The bond distances between metal and carbon atoms of an aromatic ring in **5** are slightly longer than that reported in [(N~N)Pd(η^3-CH(CH$_3$)C$_6$H$_5$)]$^+$. This is explained by the larger *trans*-influence of the phosphine situated *trans* to the π-bond in **5**.[8,10]

Table 2. Selected Bond Distances and Angles for **5**

Bond distances (Å)		Bond angles (deg)	
Pd-P1	2.228(1)	P1-Pd-N1	82.60(9)
Pd-N1	2.117(3)	N1-Pd-C4	108.9(1)
Pd-C2	2.063(4)	C4-Pd-C2	66.9(2)
Pd-C3	2.294(4)	C2-Pd-P1	99.6(1)
Pd-C4	2.363(4)	C2-Pd-N1	173.2(2)
C3-C4	1.424(6)	P1-Pd-C4	157.8(1)
C2-C3	1.457(6)	C2-C3-C4	116.6(4)
C3-C8	1.412(6)	C4-C3-C8	118.2(4)

Polymerization Test

Results of the polymerization and copolymerization of olefin and carbon monoxide catalyzed by complex **1** is summarized in Table 3. It appears that complex **1** is not a good catalyst for polymerization of olefin/carbon monoxide. The reason for low conversion is due to that the active metal center is capped with the polymer chain, i.e. one metal ion carries only one polymer chain. The metal-attached polymers were confirmed by FABMass spectrum. In addition, the intramolecular hemi-labile donor might hinder the coordination

Table 3. Copolymerization and Polymerization Catalyzed by **1**

Entry	Olefin	CO(psi)	t(h)	Yield (mg)
1	Ethylene (100 psi)	100	20	184
2	Norbornylene	50	24	40
3	Norbornylene	50	24	36
4	Styrene	50	24	41
5	Ethylene (500 psi)	-	24	48.2
6	Norbornylene	-	72	66.1

of incoming substrates, which decreases the activity of the catalyst.[6]

In summary the new designed tridentate helps us to understand the coordination behavior around the palladium metal center for catalytic polymerization. Because the extra coordinating donor hinders the incoming substrate, the catalytic activity of complex **1** on the migratory copolymerization of olefin/CO appears to be poor.

EXPERIMENTAL SECTION

General Information

All reactions, manipulations and purifications steps were performed under a dry nitrogen atmosphere. Tetrahydrofuran was distilled under nitrogen from sodium benzophenone ketyl. Dichloromethane and acetonitrile were dried over CaH_2 and distilled under nitrogen. Other chemicals and solvents were of analytical grade and were used as received unless otherwise stated.

Nuclear magnetic resonance spectra were recorded in $CDCl_3$ or acetone-d_6 on either a Bruker AC-E 200 or AM-300 spectrometer. Chemical shifts are given in parts per million relative to Me_4S for ^1H and ^{13}C NMR, and relative 85% H_3PO_4 for ^{31}P NMR. Due to the complication of aromatic region, chemical shifts of non-aromatic carbons were reported. Infrared spectra were measured on a Nicolet Magna-IR 550 spectrometer (Series-II) as KBr pallets, unless otherwise noted.

Ligand P~N~O

To (2-diphenylphospho)benzenamine (0.5 g, 1.8 mmol) was added 2-methoxylbenzadehyde (1.8 g, 1.8 mmol) in ethanol (5 mL) under nitrogen atmosphere. After stirring for 20 h, the desired compound precipitates of light yellow solids, which were filtered and washed with ice-cold ethanol several times (0.61 g, 83%): IR (KBr): 1628 ($\upsilon_{N=C}$) cm^{-1}; ^1H NMR (acetone-d_6 400 MHz): δ 8.67 (s, 1H, -N=C-H), 7.86-7.83 (m, 1H), 7.43-6.78 (m, 17H), 3.85 (s, 3H-O-CH_3); ^{31}P NMR: δ -15.0; ^{13}C NMR: δ 159.6 (-N=*C*-H), 155.0, 137.6, 134.0-124.5 (s, Ar), 120.4, 117.2, 111.4, 55.2 (s, -O-CH_3). Anal. Calcd for $C_{26}H_{22}NOP$: C, 78.97; H, 5.20; N, 3.54. Found: C, 78.78; H, 5.20; N, 3.59.

[(P~N~O)PdMe]BF_4 (1)

To a solution of [(COD)PdMeCl] (0.6 g, 2.26 mmol) in CH_2Cl_2 (5 mL) was added a dichloromethane solution (5 mL) of ligand (P~N~O) (0.9 g, 2.27 mmol) at room temperature. Another solution of $AgBF_4$ (0.42 g, 2.27 mmol) in CH_3CN (5 mL) was then added to the above mixture. After stirring for 1 h, the reaction mixture was passed through celite and the filtrate was concentrated. The solid residue was dissolved in dichloromethane/ether for crystallization. The desired complex was obtained as light yellow solids (1.32 g, 81%): IR (KBr): 1602 ($\upsilon_{N=C}$) cm^{-1}; ^1H NMR (acetone-d_6, 400 MHz): δ 9.53 (s, 1H, -N=C-H), 8.28 (m, 1H, Ar), 8.10 (m, 1H, Ar), 7.78-7.30 (Ar, 16H), 4.25 (s, 3H, -OCH_3), 0.60 (d, J_{P-H} = 0.6 Hz, 3H, Pd-CH_3); ^{31}P NMR: δ 42.0; ^{13}C NMR: δ 165.3 (-N=*C*-H), 158.4, 153.9, 135.7-127.4 (s, Ar), 122.5, 119.0, 113.7, 59.4 (s, O-*Me*), -0.3 (Pd-*C*H_3). Anal. Calcd for $C_{27}H_{25}BF_4NOPPd$: C, 53.72; H, 4.17; N, 2.32. Found: C, 53.34; H, 4.49; N, 2.08.

[(P~N~O)PdCOMe]BF_4 (2)

Complex **1** (30 mg, 0.5 mmol) in dichloromethane (10 mL) was pressurized with CO for (150 psi) for 30 min. The solution was passed through celite to remove some palladium black. Diethyl ether was added to the filtrate to precipitate the desired complex as yellow solids (25 mg, 74%): IR (KBr): 1621 ($\upsilon_{N=C}$), 1713 ($\upsilon_{C=O}$) cm^{-1}; ^1H NMR (acetone-d_6, 400 MHz): δ 9.37 (d, J_{P-H} = 1 Hz, 1H, -N=C-H), 8.42 (m, 1H, Ar), 7.82-7.28 (m, 17H, Ar), 4.08 (s, 3H, -OCH_3), 2.18 (s, 3H, Pd-$COCH_3$); ^{31}P NMR: δ 20.7; ^{13}C NMR: δ 222.7 (*C*=O), 166.7 (-N=*C*-H), 159.4, 154.1, 134.1-112.4 (Ar), 56.1 (s, O-*Me*), 35.2 (Pd-*C*H_3). FABMS (M-BF_4) *m/z* for [$C_{28}H_{25}NO_2PPd$] = 544.10 (calcd. 544.07).

[(P~N~O)PdCH_2CH_2COMe]BF_4 (3)

A solution of **1** (30 mg, 0.5 mmol) in dichloromethane (10 mL) was bubbled with carbon monoxide for 30 min followed by ethylene gas for another 30 min. The resulting mixture was concentrated and the residue was dissolved in dichloromethane. Ether was added to that solution to give the desired inserted product as yellow solids (26 mg, 79%): IR (KBr): 1602 ($\upsilon_{N=C}$), 1635 ($\upsilon_{C=O}$) cm^{-1}; ^1H NMR (acetone-d_6, 400 MHz): δ 9.40 (s, 1H, -N=C*H*-), 8.55 (m, 1H), 7.72-6.94 (m, 17H), 3.92 (s, 3H), 3.06 (m, 2H), 2.15 (s, 3H), 1.82 (m, 2H); ^{31}P NMR: δ 37.6; ^{13}C NMR: δ 232.9 (*C*=O), 165.6 (-N=*C*-H), 160.0, 154.9-111.1 (Ar-*C*), 55.9 (-O-*C*H_3), 50.3, 37.5, 21.3. Anal. Calcd for $C_{30}H_{29}$ BF_4NO_2PPd: C, 54.61; H, 4.43; N, 2.12. Found: C, 54.72; H, 4.21; N, 2.08.

[(P~N~O)PdCH(Ph)CH_2COMe]BF_4 (4)

The procedure for preparation of this compound is similar to that for **3**, except styrene was used instead of ethylene. Complex **4** is a yellow solid (87%): IR (KBr): 1602 (υ_{C+N}), 1635 (υ_{C+O}) cm^{-1}; ^1H NMR ($CDCl_3$ 400 MHz): δ 9.30 (d, *J* = 1.64 Hz, 1H, -N=C-H), 8.81 (m, 1H), 7.56-6.65 (m, 22H), 3.92 (s, 3H), 3.59-3.52 (dd, *J* = 7.7, 20 Hz, 1H), 3.20 (m, 1H),

2.94 (m, J = 20 Hz, 1H), 2.31 (s, 3H-CO-CH_3); ^{31}P NMR: δ 31.33; ^{13}C NMR: δ 232.9 (*C*=O), 164.4 (-N=CH-), 160.4, 154.1-111.6 (Ar), 55.9 (-O-*C*H_3), 50.3, 44.72, 44.68, 27.9 (-CO-*C*H_3). Anal. Calcd. for $C_{36}H_{33}BF_4NO_2PPd$: C, 58.76; H, 4.52; N, 1.90. Found: C, 58.65; H, 4.25; N, 1.79.

[(P~N~O)Pd(η^3-CH(CH_3CH_2)C_6H_5)]BF_4 (5)

Pre-distilled styrene (1 mL) was added to a solution of complex **1** (30 mg, 0.5 mmol) in dichloromethane (10 mL). After stirring at room temperature for 24 h, the reaction mixture was passed through celite to remove some palladium black. The desired complex was precipitated by addition of diethyl ether to the filtrate. Upon filtration, complex **5** is obtained as yellow solids (23.6 mg, 67%): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.03 (d, J = 2.4 Hz, 1H, -N=C-H), 7.73-6.86 (23H, Ar), 3.84 (s, 3H), 3.54 (m, J = 6.7 Hz, 1H), 1.25 (dd, 1H, $J_{H\text{-}H}$ = 6.7 Hz, $J_{P\text{-}H}$ = 5.6 Hz); ^{31}P NMR: δ 31.2; ^{13}C NMR (-25 °C): δ 165.1 (-N=*C*H-), 159.4, 155.3, 135.2-119.4 (Ar), 110.7, 55.9 (d, $J_{P\text{-}H}$ = 26 Hz, Ph-*C*H-), 53.8 (O-*Me*), 16.0 (-*C*H_3). Anal. Calcd. for $C_{34}H_{31}BF_4NOPPd$: C, 58.86; H, 4.50; N, 2.02. Found: C, 58.66; H, 4.22; N, 1.97.

Copolymerization

To a stainless-steel autoclave (500 mL) the catalyst **1** (30 mg, 0.5 mmol) and olefin were introduced by dissolving in CH_2Cl_2 (70 mL). The reaction mixture was then pressurized with a mixture of CO and stirred at constant temperature. Reaction was stopped after the specified time, and the resulting white solid was collected and washed with 5 N HCl followed by water and acetone. The copolymers obtained were characterized by NMR spectroscopy.

X-ray Crystallographic Analysis

A single crystal suitable for X-ray determination was obtained for **5** by slow diffusion of hexane into a dichloromethane solution at room temperature. Cell parameters were determined either by a Siemens SMART CCD or a CAD-4 diffractometer. Crystal data: $C_{36}H_{35}BCl_4F_4NOPPd$, MW = 863.63, T = 150 K, monoclinic, $P2_1/c$, a = 12.2000(2), b = 13.4306(2), c = 22.6699(3), α = 90°, β = 91.7742(8), γ = 90°, Z = 4, V = 3712.8(1) Å^3, F(000) 1744, 0.40 × 0.32 × 0.08 mm, reflection collected 58207, reflection 8524 (R_{int} = 0.0772), R1 = 0.0512, wR2 = 0.1285 for [I > 2σ(I)]. ORTEP plot is illustrated in Fig. 1 (Labels of phenyl groups are omitted for clear view, 30% probability ellipsoids depicted).

Supplementary Material

Atomic coordinates, isotropic and anisotropic thermal parameters, and bond distances and angles for **5** are available from the corresponding author.

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