Electrophilic Binuclear Methylpalladium(II) Complexes: Copolymerization of Alkenes and Carbon Monoxide

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Received April 2, 2001

Reaction of $[PdMe_2(\mu\text{-pyd})]_2$ (pyd = pyridazine) with the bis(bidentate) ligands *R,R/S,S-trans*-1,2-C_6H_{10}(N=CH-2-$C_5H_4N)_2$, **1**, or C_2H_4(N=CH-2-$C_5H_4N)_2$, **2**, gave the binuclear dimethylpalladium(II) complexes *R,R/S/S-trans*-1,2-$[C_6H_{10}\{N{=}CH\text{-}2\text{-}C_5H_4N(PdMe_2)\}_2]$, **3**, or $[C_2H_4\{N{=}CH\text{-}2\text{-}C_5H_4N(PdMe_2)\}_2]$, **4**, respectively. Complex **3** is C_2-symmetric. Reaction of **3** or **4** with 2 equiv of $[H(OEt_2)_2][BAr'_4]$, Ar′ = 3,5-$(CF_3)_2C_6H_3$, in acetonitrile, gave methane and the electrophilic binuclear complexes *R,R/S,S-trans*-1,2-$[C_6H_{10}\{N{=}CH\text{-}2\text{-}C_5H_4N(PdMe(NCMe))\}_2][BAr'_4]_2$, **5**, and $[C_2H_4\{N{=}CH\text{-}2\text{-}C_5H_4N(PdMe(NCMe))\}_2][BAr'_4]_2$, **6**, by methylpalladium bond protonolysis. Complexes **5** and **6** could be converted to the acyl complexes *R,R/S,S-trans*-1,2-$[C_6H_{10}\{N{=}CH\text{-}2\text{-}C_5H_4N(Pd(NCMe)(COMe))\}_2][BAr'_4]_2$, **7**, and $[C_2H_4\{N{=}CH\text{-}2\text{-}C_5H_4N(Pd(NCMe)(COMe))\}_2][BAr'_4]_2$, **8**, in the presence of carbon monoxide and were found to be catalyst precursors for the copolymerization of styrene or 4-methylstyrene with carbon monoxide. Copolymerization reactions catalyzed with optically pure *R,R*-**5*** and achiral **6** were carried out at room temperature and pressure to give polyketones, whose chiral microstructures are described.

Introduction

Electrophilic complexes of the late transition metals are of interest because of their catalytic potential in processes such as C−H bond activation and olefin polymerization.[1,2] For example, the alternating copolymerization of olefins with carbon monoxide to give polyketones has been catalyzed by many different electrophilic palladium(II) complexes.[3,4] Of particular interest is the copolymerization of vinyl monomers with carbon monoxide since this process gives rise to true stereocenters within the polymer backbone.[4] A high molecular weight polyketone with syndiotactic microstructure is optically inactive because of the alternation of chirality in the carbon stereocenters (...*RSRSRS*...). Polymers in which the ratio $R/S \neq 1$ are chiral and are expected to be optically active if formed using an enantiomerically pure catalyst.[5−7] For example, palladium(II) complexes with C_2-symmetric bis(oxazoline) ligands can give perfectly alternating copolymers of CO with styrene,[5] 4-methylstyrene,[5] or 4-*tert*-butylstyrene[6] having very high degrees of isotacticity. C_1-symmetric P,N hybrid ligands have been employed to synthesize more robust palladium(II) catalysts which give isotactic polyketones from styrene and carbon monoxide.[7] Similar complexes have also been used to study insertion intermediates in olefin/carbon monoxide copolymerization.[8] It is also possible to obtain optically active polyketones with predominantly syndiotactic microstructure by using unsymmetrical, chiral diimine palladium(II) complexes as catalysts.[9]

There is limited literature on the use of binuclear palladium(II) complexes as catalysts for forming polyketones (none using diimine ligands), and it was of interest

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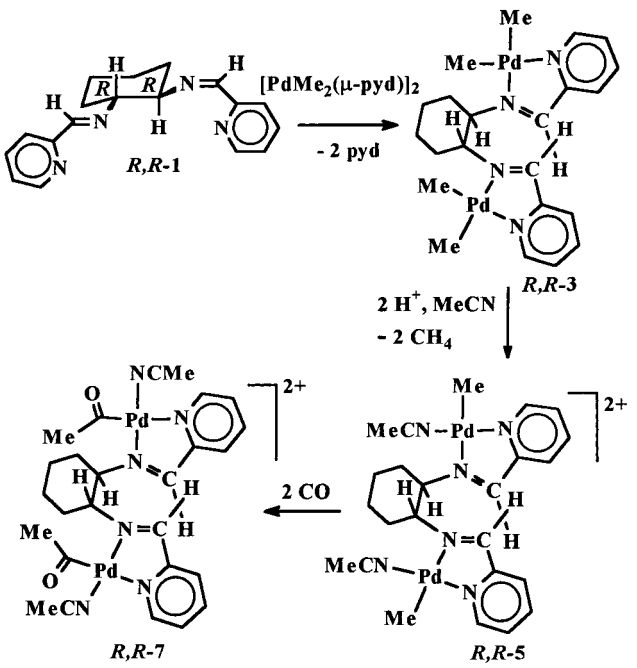
10.1021/om0102706 CCC: $20.00
Publication on Web 06/30/2001

Scheme 1



to study such systems to determine if cooperative effects might occur.[10] This article reports that bis{palladium(II)} complexes derived from the bis(bidentate) ligands *R,R/S,S-trans*-1,2-C_6H_{10}(N=CH-2-C_5H_4N)$_2$, **1**, or C_2H_4-(N=CH-2-C_5H_4N)$_2$, **2**, can give active copolymerization catalysts and reports on the stereoselectivity of the catalytic reactions.

Results

Synthesis and Reactions of *R,R/S,S-trans*-1,2-[C_6H_{10}{N=CH-2-C_5H_4N(PdMe$_2$)}$_2$], 3. The synthesis of complexes **3**, **5**, and **7** is outlined in Scheme 1. Both racemic (*R,R/S,S*) and enantiopure (*R,R*-**3***, -**5***, and -**7***) complexes were prepared.

The reaction of the bis(bidentate) ligand *R,R/S,S-trans*-1,2-C_6H_{10}(N=CH-2-C_5H_4N)$_2$, **1**, with [PdMe$_2$(μ-pyd)]$_2$, pyd = pyridazine, gave *R,R/S,S-trans*-1,2-[C_6H_{10}-{N=CH-2-C_5H_4N(PdMe$_2$)}$_2$], **3**, which is C_2-symmetric and chiral. The ^{1}H NMR spectrum of **3** contained two sharp singlets at δ(MePt) = 0.28 and 0.30, corresponding to methyl ligands that are *trans* to either pyridyl or imine groups, and a single imine resonance at δ(CH) = 8.70, consistent with the proposed C_2-symmetry for **3**. The corresponding dimethylplatinum(II) analogue of **3** is known and was shown to exist as a 2:1 mixture of *anti,anti* and *syn,syn* conformers, arising from restricted rotation about the cyclohexyl C−N bonds (eq 1).[11] There is no evidence for similar behavior with complex **3**, whose ^{1}H NMR resonances remain sharp and unsplit at temperatures down to −80 °C. Hence, either there is one dominant conformer of **3** or rotation about the N−C bonds is rapid in the palladium complex even at low temperature. A structure determination showed that the racemic palladium complex *R,R/S,S*-**3** exists in the *anti,anti* conformation in the solid state.

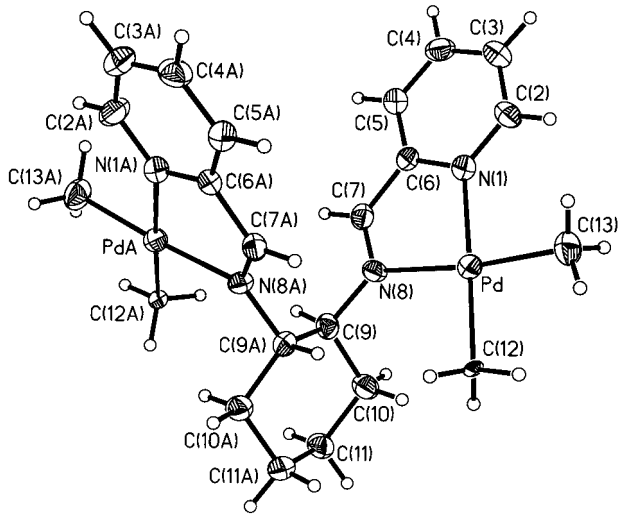
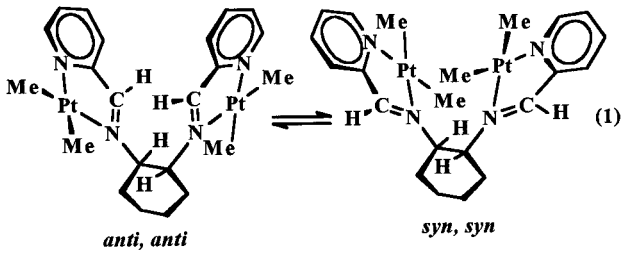


Figure 1. Molecular structure of complex **3** with 35% probability thermal ellepsoids.



The molecular structure of complex **3** is given in Figure 1, and selected bond distances and angles are given in Table 1. The structure confirms that the binuclear complex has crystallographic C_2 symmetry, with each dimethylpalladium(II) unit bound to an imine/pyridyl chelate and with the cyclohexane ring in the chair conformation. The conformation with respect to rotation about the N(8)−C(9) bonds is such that the methyl ligand on each palladium(II) center is *anti* with respect to the cyclohexyl NCH groups. This is presumably to minimize steric interactions, and the conformation adopted by complex **3** is the major conformation proposed, but not proven crystallographically, for the analogous platinum(II) complex.[11] The *anti,anti* conformation of complex **3** allows the palladium centers to be well separated at 6.19 Å.

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Table 1. Selected Bond Lengths and Angles for Complex 3[a]

(a) Bond Lengths (Å)			
Pd−C(13)	2.035(4)	Pd−C(12)	2.100(3)
Pd−N(1)	2.119(4)	Pd−N(8)	2.189(3)
N(1)−C(2)	1.334(5)	N(1)−C(6)	1.357(5)
C(2)−C(3)	1.394(6)	C(3)−C(4)	1.378(6)
C(4)−C(5)	1.375(5)	C(5)−C(6)	1.379(5)
C(6)−C(7)	1.476(5)	C(7)−N(8)	1.266(5)
N(8)−C(9)	1.470(5)	C(9)−C(10)	1.529(5)
C(9)−C(9A)	1.553(7)	C(10)−C(11)	1.516(5)
C(11)−C(11A)	1.535(7)		
(b) Bond Angles (deg)			
C(13)−Pd−C(12)	85.41(14)	C(13)−Pd−N(1)	94.38(15)
C(12)−Pd−N(1)	176.73(12)	C(13)−Pd−N(8)	171.65(14)
C(12)−Pd−N(8)	102.87(11)	N(1)−Pd−N(8)	77.42(11)
N(8)−C(7)−C(6)	120.4(3)	C(7)−N(8)−C(9)	116.4(3)
C(7)−N(8)−Pd	112.6(2)	C(9)−N(8)−Pd	131.0(2)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x+1/2, -y+1/2, z$; #2 $-x+3/2, -y+1/2, z$.

Addition of 2 equiv of $[H(OEt_2)_2][BAr'_4]$ (Ar′ = 3,5-$(CF_3)_2C_6H_3$) to a solution of complex **3** in CH_3CN gave *R,R/S,S-trans*-1,2-$[C_6H_{10}\{N{=}CH\text{-}2\text{-}C_5H_4N(PdMe(NCCH_3))\}_2][BAr'_4]_2$, **5**, by protonolysis of one methylpalladium bond in each dimethylpalladium(II) unit. The ^1H NMR spectrum of **5** contained one methylpalladium resonance at $\delta = 1.12$ and one imine resonance at $\delta = 8.63$, respectively. The proton spectrum remained unchanged with sharp resonances down to −40 °C. In the ^{13}C NMR spectrum, recorded at −40 °C, the resonances for the methylpalladium and imine groups appeared at $\delta = 1.6$ and 166.6, respectively. The NMR spectra thus show that the C_2-symmetry of the substrate is present even at low temperature, and so it is established that the product is formed in a selective manner (Scheme 1). The $^1H-^1H$ ROESY spectrum for complex **5** showed strong NOEs between the MePd protons and the NCH protons of the pyridyl groups, proving that the methyl and pyridyl ligands are mutually *cis*. If the selectivity is determined by kinetic control, it is the methylpalladium group *trans* to the pyridyl group that is selectively cleaved (Scheme 1).

The reaction of complex **5** in CD_3CN solution with CO at room temperature gave the complex *R,R/S,S-trans*-1,2-$[C_6H_{10}\{N{=}CH\text{-}2\text{-}C_5H_4N(Pd(COMe)(NCCD_3))\}_2][BAr'_4]_2$, **7**, by insertion of CO into each methylpalladium(II) bond (Scheme 1). The ^1H and ^{13}C NMR spectra of **7** showed that the complex has C_2-symmetry. The *Me*COPd group gave a singlet at $\delta = 2.5$ in the ^1H NMR spectrum and at $\delta = 34.2$ in the ^{13}C NMR spectrum. To confirm the position of the acyl ligand, 1-D, $^1H-^1H$ ROESY correlation spectroscopy was carried out. Strong NOEs were observed between the acyl methyl group and the cyclohexyl protons but not with the aryl protons, and so it is deduced that the acyl ligand is *trans* to the pyridyl ligand, with the stereochemistry shown in Scheme 1. The stereochemistry is the one expected if insertion of carbon monoxide into the Pd−alkyl bonds occurs by migration of the hydrocarbyl group to the unsaturated CO ligand (Scheme 1).[8d,e] However, it is not proved that the stereochemistry is determined by kinetic rather than thermodynamic factors.

Attempts were made to study the reaction of **7** with styrene to characterize the next step in the potential copolymerization, but complex mixtures were formed and no further pure complexes could be characterized.

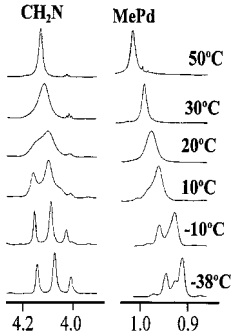
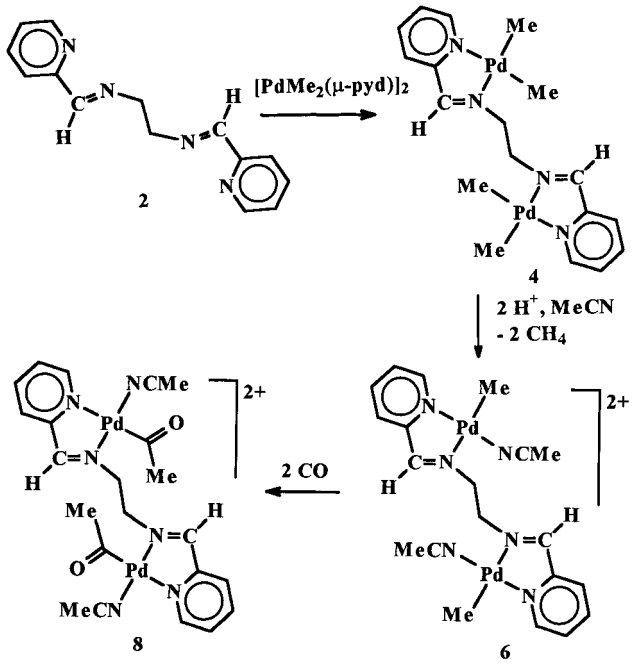


Figure 2. Variable-temperature ^1H NMR spectra for complex **6** showing only the CH_2N and MePd resonances. The fast exchange region has been almost reached at +50 °C.

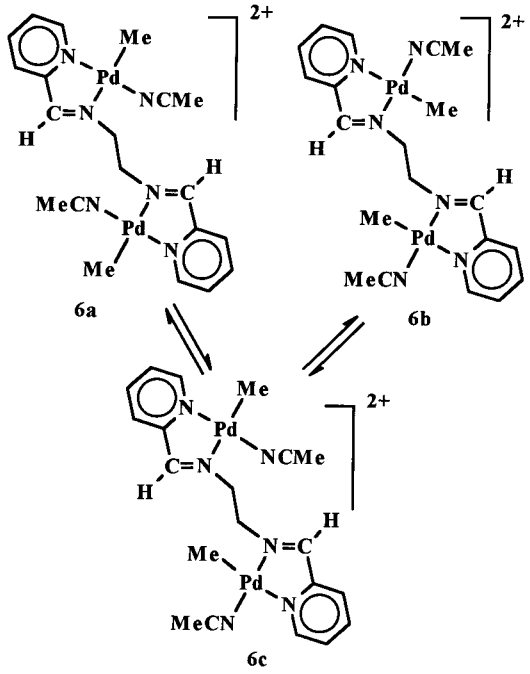
Scheme 2



Synthesis and Reactions of $[C_2H_4\{N{=}CH\text{-}2\text{-}C_5H_4N\text{-}(PdMe_2)\}_2]$, 4. The synthesis of complexes **4**, **6**, and **8** is outlined in Scheme 2. The chemistry is similar to that in Scheme 1, but the product complexes **4**, **6**, and **8** are of course achiral. The ^1H NMR of complex **4** contained two methyl resonances and one imine resonance as expected, and the resonances remained sharp at −80 °C. The C_{2h}-symmetric conformation shown in Scheme 2 is expected to be favored due to steric considerations.

The room-temperature ^1H NMR spectrum of complex **6** was consistent with a C_{2h}-symmetric complex and proved that one methylpalladium group had been cleaved from each dimethylpalladium(II) unit during the protonolysis of complex **4**. There was a single methylpalladium resonance at $\delta = 0.99$ and single resonances for the CH_2N and imine (CH=N) resonances at $\delta = 4.12$ and 8.52, respectively, but the broad peaks indicated fluxionality (Figure 2). At lower temperatures, the resonances became broader, and at 10 °C the methylene singlet had split into two broad peaks (Figure 2). The imine resonance and two of the aromatic resonances also split at 10 °C. At 0 °C the methylpalladium resonance split into two peaks at $\delta = 0.96$ and 0.99, and at −10 °C three methylene resonances were resolved at $\delta =$

Scheme 3



4.04, 4.11, and 4.18. Three methylpalladium and imine resonances were resolved at −20 °C, and no further splitting occurred on cooling to the lowest temperature possible in acetonitrile solvent (−38 °C). The spectral changes were reversible and the fast exchange limit was almost reached at 50 °C, as indicated by sharper resonances. Figure 2 also illustrates the temperature dependence of the chemical shift of the MePd resonances. At room temperature, the ^{13}C NMR spectrum of **6** already showed two broad resonances each for the imine and pyridyl C-2 carbons (see Experimental Section). All the other ^{13}C resonances were broad at this temperature, but at −35 °C several of the resonances split into four lines. For example, the imine (CH═N) region featured resonances at δ = 167.7, 168.5, 174.1, and 174.6. These results suggest the presence of three rapidly equilibrating isomers, two of which (**6a**, **6b**) are C_{2h} symmetric and so have one imine resonance each and one which (**6c**) is C_s symmetric and has two imine resonances (Scheme 3). Some of the resonances are presumed to be degenerate in the ^{1}H NMR spectra (Figure 2), since only three distinct methylpalladium environments were resolved. This appears to be the first report of this type of fluxionality for nitrogen-donor complexes of the type [(N−N′)PdMe(NCMe)]$^+$, but an unspecified fluxionality has been suggested for related unsymmetrical phosphine-indole complexes [(P−N)PdMe(NCMe)]$^+$, P−N = 1,3-C_6H_4-(PR_2)(C═NCHRCH_2O).[12]

Complex **6** reacted easily with carbon monoxide to give 1,2-[C_2H_4{N═CH-2-C_5H_4N(Pd(COMe)(NCCD$_3$))}$_2$]-[BAr′$_4$]$_2$, **8**, by insertion of CO into both methylpalladium bonds. At room temperature the ^{1}H NMR spectrum of **8** was consistent with a C_{2h}-symmetric complex, since at 20 °C only a single sharp resonance was present for the acyl methyl group at δ = 2.49. Broadening of this methyl group resonance began at 0 °C, at −20 °C

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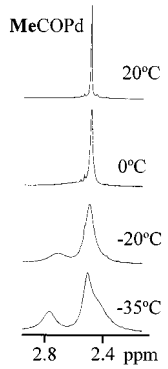
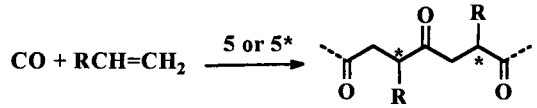


Figure 3. Variable-temperature ^{1}H NMR spectra for complex **8** showing only the acylpalladium resonances.

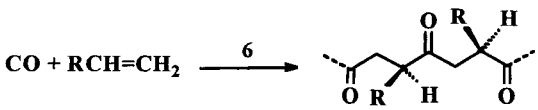
there were two acyl-methyl resonances at δ = 2.50 and 2.75 in a 5:1 ratio, and at −35 °C there were three broad resonances at δ = 2.42, 2.51, and 2.80, but the slow exchange region was not reached at −40 °C (Figure 3). The methylene and aromatic resonances were all broad at −40 °C. These spectra indicate fluxionality of the kind established for complex **6** but with a somewhat lower activation energy such that the fluxionality was not frozen out at −40 °C. A 2-D, ^{1}H−^{1}H NOESY experiment was carried out for complex **8** and featured strong correlations of the acyl methyl group with the methylene protons, but not with the aromatic protons. Hence the major isomer is suggested to have the stereochemistry with the acyl ligands predominantly in sites *trans* to the pyridyl donors, as shown in Scheme 2.

Copolymerization Reactions. Complexes **5** and **6** are yellow brown solids that are soluble in styrene and 4-methylstyrene, thus allowing polymerizations to be carried out in neat monomer. When carbon monoxide was passed through a yellow solution of either **5** or **6** in styrene or 4-methylstyrene at room temperature and pressure, the solution became viscous and addition of MeOH precipitated the copolymer as a white solid (eqs 2 and 3). When polymerizations were carried out for extended periods, some metallic palladium was formed by degradation of the catalyst and was removed by filtration prior to precipitation of the polymer.



(2)

9a, **9a***, R = C_6H_5
9b, **9b***, R = 4-MeC_6H_4



(3)

10a, R = C_6H_5
10b, R = 4-MeC_6H_4

Copolymers **9a** and **9b**, prepared using racemic complex **5** (eq 2) were highly soluble in common organic solvents, and the ^{1}H and ^{13}C NMR spectra were in good agreement with reported examples of strictly alternating head-to-tail styrene/CO or 4-methylstyrene/CO copolymers.[3p,9,3l] The ^{13}C NMR spectrum for copolymer **9a** contained *ipso*-carbon resonances attributed to the four triad structures, *RSR*/*SRS*, *RSS*/*SRR*, *RRS*/*SSR*,

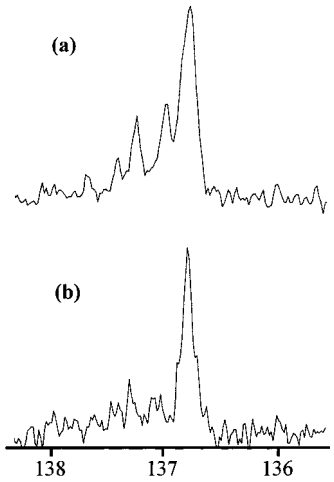


Figure 4. ^{13}C NMR spectra in the *ipso*-carbon region only of (a) copolymer **9a** and (b) copolymer **10a**.

and *RRR*/SSS at δ = 136.7, 136.9, 137.2, and 137.4, respectively (Figure 4a).[3p,9,3l] The relative intensity of each triad resonance indicates a microstructure that is ca. 50% syndiotactic, the balance being mostly atactic microstructure with only a minor amount of isotactic microstructure (*RSR*/*SRS* = 50%, *RSS*/*SRR* = 20%, *RRS*/*SSR* = 20%, *RRR*/*SSS* = 10%).[9] In the carbonyl region of the ^{13}C NMR spectrum, the main resonance at δ = 206.3 was accompanied by two resolved secondary peaks at δ = 205.9 and 206.7, thus confirming the low degree of stereoregularity in **9a**. Similar stereoregularity was observed for the copolymerization of 4-methylstyrene and CO using racemic complex **5**. The optically active polymers **9a*** and **9b*** were prepared using enantiomerically pure *R*,*R*-*trans*-1,2-[C_6H_{10}{N=CH-2-C_5H_4N(PdMe(NCCH$_3$))}$_2$][BAr′$_4$]$_2$, **5***, and gave $[\alpha]_D^{25}$ = −22° (*c* 1.6 mg/mL) and −33° (*c* 2.4 mg/mL), respectively. The polymers were formed at 1.7 × 10^3 and 3.9 × 10^3 g polymer/(mol catalyst·h) (room temperature, 1 atm CO) for **9a** and **9b**, respectively, and the molecular weights were low: **9a**, M_w = 5120, M_w/M_n = 1.62; **9b**, M_w = 4780, M_w/M_n = 1.58.

The copolymers **10a** and **10b** were prepared by using the achiral complex **6** as catalyst (eq 3), and the polymers had distinctive properties when compared to **9a** and **9b**, which were prepared using the chiral catalyst **5**. The differences can be seen by comparing the *ipso*-carbon resonances in the ^{13}C NMR spectrum of **10a** (Figure 4b) with those of **9a** (Figure 4a). The clearly weaker intensities of the secondary peaks in the ^{13}C NMR of **10a** indicate a higher percentage of syndiotactic microstructure and so a significant increase in stereoregularity relative to **9a**. The ^1H NMR spectra of **10a** and **10b** had sharper resonances compared to **9a** and **9b**, with some fine structure resolved (for example, doublet of doublet resonances at δ = 2.60 and 3.12 for diastereotopic CH_2 protons of **10a**), confirming the more regular syndiotactic microstructure.[9] Since complex **5** is achiral, a chain end control mechanism must give rise to the high stereoregularity; this mechanism has been invoked previously to explain the formation of highly syndiotactic polyketone with many achiral mononuclear catalysts.[3s,t,9,13]

The polymers **10a** and **10b** were far less soluble than **9a** and **9b**, implying greater molecular weights and stereoregularity, but making it difficult to obtain molecular weight data. The complex **6** is a more active catalyst than **5**, but polymer yields are still limited by catalyst decomposition; productivities were 3.9 × 10^3 and 3.1 × 10^4 g polymer/(mol catalyst·h) for **10a** and **10b**, respectively, at room temperature and 1 atm of CO. The molecular weight of **10a** was M_w = 22 500 with M_w/M_n = 1.49, but **10b** was insufficiently soluble in THF for molecular weight measurement.

Discussion

The protonolysis of one methyl group from each dimethylpalladium(II) center appears to occur selectively for complex **3** but not for complex **4**.[11] This difference in selectivity can be attributed to the different steric environments at palladium(II) for the chiral and achiral ligand systems. Since isomerism occurs very easily, at least in the case of the complex **5**, the isomer ratio is thought to be determined by thermodynamic effects that are probably steric in origin. Thus, for the chiral complex **3**, it appears that the methyl group adjacent to the bulky cyclohexyl group is cleaved selectively, but it is also possible that the other methyl group is cleaved followed by rapid isomerization to give **5**. The three possible isomers of complex **6** (Scheme 3) have similar energies, as is clearly shown by the NMR spectra of Figure 2. This is presumably a result of similar steric environments *cis* to the pyridyl and imine groups, and the NMR study shows that the isomers equilibrate rapidly. Several mononuclear square-planar palladium(II) complexes of the type [(N−N′)PdClMe] and [(N−N′)Pd(NCMe)Me]$^+$ that are supported by unsymmetrical diimine ligands are known to form in a selective manner.[14,15] In the chloro complexes, the chloride ligand is *cis* to the smaller imine group, while in the acetonitrile complexes, the methyl group is *cis* to the smaller imine group.[14,15]

For platinum and palladium complexes based on ligand **1**, the metal centers can be close together or widely separated depending on the conformation about the N−C bonds.[4,11] Cooperative effects between the two palladium centers might be expected if the metals are close,[16] but they are widely separated in complex **3**, which has *d*(Pd−Pd) = 6.19 Å (Figure 1). Under these circumstances, the metal centers can act independently, and this appears to be the case in the reaction chemistry of complexes **5** and **6**.

The stereoselectivity observed for the copolymerization reactions catalyzed by **5** and **6** was very similar to that reported for related mononuclear systems. Catalysts of the type [(N−N′)PdMe(NCMe)]$^+$, which are supported by asymmetric chiral diimine ligands N−N′, gave lower stereoregularity than catalysts based on

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symmetric ligands in the product polyketones.[6,9] In another systematic study it was shown that bulkier supporting ligands gave lower selectivity for formation of syndiotactic styrene/CO copolymers, and the effect was attributed to a disruption of π,π interactions between the ligand and the incoming olefin.[9] Complex **5**, which is based on 1,2-diaminocyclohexane, is more sterically encumbered than is complex **6**, and this leads to reduced stereoregularity of polymers **9** relative to **10**. Further, it has been shown, using catalysts supported by a chiral diimine ligand, that an increase in isotacticity accompanies a decrease in syndiotacticity since chiral induction from the ligand begins to compete with the chain end control mechanism.[9] The optical activity found for **9a*** and **9b*** is consistent with these precedents. Thus, in this first study of alkene/CO copolymerization with chiral or achiral binuclear palladium(II) complexes, it seems that the two palladium centers act essentially independently in the catalysts **5** and **6**.

Experimental Section

General Procedures. All reactions were carried out under an N_2 atmosphere using standard Schlenk techniques or using a drybox. All solvents were dried and distilled prior to use. ^{1}H and ^{13}C NMR spectra were recorded by using a Varian Gemini 300 Mz or Inova 600 MHz spectrometer. ^{1}H−^{1}H ROESY or NOESY experiments and variable-temperature experiments were recorded using the 600 MHz spectrometer. Chemical shifts are reported relative to TMS. IR spectra were recorded as Nujol mulls or thin films in the range 4000−400 cm^{-1} using a Perkin-Elmer 2000 FT-IR instrument. Optical rotation measurements were performed on a Autopol III automatic polarimeter using a sodium lamp. Molecular weights and molecular weight distributions of polymers were measured by gel permeation chromatography using THF as the solvent, and standard polystyrene samples were used for calibration. The ligands *R,R/S,S-trans*-1,2-C_6H_{10}(N=CH-2-C_5H_4N)$_2$, **1**, *R,R-trans*-1,2-C_6H_{10}(N=CH-2-C_5H_4N)$_2$, **1***, and C_2H_4(N=CH-2-C_5H_4N)$_2$, **2**, were prepared as described previously.[16,17] The compounds [$PtMe_2(\mu$-$SMe_2)]_2$,[18] [$PdMe_2(\mu$-pyridazine)]$_2$,[19] and [$H(OEt_2)_2$][BAr′$_4$] (Ar′ = 3,5-$(CF_3)_2C_6H_3$),[20] were prepared by the literature methods.

R,R/S,S-trans*-1,2-[C_6H_{10}{N=CH-2-C_5H_4N(PdMe$_2$)}$_2$] (3).** To a solution of *R,R/S,S-trans*-1,2-C_6H_{10}(N=CH-2-C_5H_4N)$_2$, **1** (0.167 g, 0.57 mmol), in diethyl ether (10 mL) was added [$PdMe_2(\mu$-pyd)]$_2$ (0.23 g, 0.57 mmol) to give an orange solution, from which the bright orange product precipitated after several minutes. The mixture was stirred for 15 h, and then the product was isolated by filtration, washed with diethyl ether (3 × 8 mL), and dried under vacuum. Yield = 0.29 g (90%). Anal. Calcd for $C_{22}H_{32}N_4Pd_2$: C, 46.7; H, 5.7; N, 9.9. Found: C, 46.9; H, 5.7; N, 10.1. ^{1}H NMR (CD_2Cl_2): δ 0.28 [s, 6H, Pd-Me]; 0.30 [s, 6H, Pd-Me]; 1.50 [m, 2H]; 1.9 [br m, 6H]; 4.4 [m, 2H, NCH]; 7.45 [m, 2H]; 7.64 [m, 2H]; 7.86 [t d, 2H]; 8.57 [d, 2H]; 8.70 [s, 2H, N=CH]. The optically pure complex *R,R-trans*-1,2-[C_6H_{10}{N=CH-2-C_5H_4N(PdMe$_2$)}$_2$], **3, was prepared similarly, but from chiral ligand *R,R-trans*-1,2-C_6H_{10}(N=CH-2-C_5H_4N)$_2$, **1***.

[C_2H_4{N=CH-2-C_5H_4N(PdMe$_2$)}$_2$] (4) was prepared similarly from ligand C_2H_4(N=CH-2-C_5H_4N)$_2$, **2**, and [$PdMe_2(\mu$-pyd)]$_2$. Yield = 71%. Anal. Calcd for $C_{18}N_{26}N_4Pd_2$: C, 42.3; H, 5.1; N, 11.0. Found: C, 42.2; H, 5.3; N, 10.6. ^{1}H NMR (CD_2Cl_2): δ 0.024 [s, 6H, Pd-Me]; 0.026 [s, 6H, Pd-Me]; 4.27 [s, 4H, CH_2]; 7.52 [m, 4H]; 7.85 [m, 2H]; 8.48 [s, 2H, N=CH]; 8.64 [m, 2H].

***R,R/S,S-trans*-1,2-[C_6H_{10}{N=CH-2-C_5H_4N(PdMe(NCCH$_3$))}$_2$][BAr′$_4$]$_2$ (5).** To a solution of **3** (0.028 g, 0.50 mmol) in CH_3CN (5 mL) at 0 °C was added [$H(OEt_2)_2$][BAr′$_4$] (Ar′ = 3,5-$(CF_3)_2C_6H_3$) (0.11 g, 0.11 mmol) in CH_3CN (5 mL), causing a color change from orange to green-yellow. After 4 min, the solvent was removed under reduced pressure to give a pale yellow powder. Yield = 0.096 g (83%). Anal. Calcd for $C_{88}H_{56}B_2F_{48}N_6Pd_2$: C, 45.1; H, 2.4; N, 3.6. Found: C, 45.2; H, 2.5; N, 3.4. ^{1}H NMR (acetone-d_6): δ 1.20 [s, 6H, Pd-Me]; 1.58 [br m, 2H]; 1.90−2.2 [br m, 6H]; 2.80 [s, 6H, Pd-NCCH$_3$]; 4.35 [m, 2H, NCH]; 7.66 [m, 8H, BAr′$_4$]; 7.78 [m, 16H, BAr′$_4$]; 7.88 [m, 2H, pyr H-5]; 8.18 [d, 2H, pyr H-3]; 8.34 [m, 2H, pyr H-4]; 8.66 [d, 2H, pyr H-6]; 9.11 [s, 2H, N=CH]. ^{1}H NMR (CD_3CN): δ = 1.12 [s, 6H, Pd-Me]; 1.40 [br m, 2H]; 1.70−2.05 [br m, 6H]; 3.95 [m, 2H, NCH]; 7.66 [m, 8H, BAr′$_4$]; 7.60 [m, 16H, BAr′$_4$]; 7.73 [m, 2H, pyr H-5]; 7.93 [d, 2H, pyr H-3]; 8.23 [m, 2H, pyr H-4]; 8.46 [d, 2H, pyr H-6]; 8.63 [s, 2H, N=CH]; resonances due to PdNC*Me* were not observed in CD_3CN due to exchange with the solvent. ^{1}H−^{1}H ROESY (CD_3CN, −35 °C) correlations for **5**: δ 8.46 [pyr H-6] with δ 1.12 [Pd-Me] and δ 7.73 [pyr H-5]; δ 1.12 [Pd-Me] with δ 8.46 [pyr H-6] only; δ 8.63 [N=CH] with δ 7.93 [pyr H-3] and δ 3.95 [NCH]; δ 8.23 [pyr H-4] with δ 7.73 [pyr H-5] and δ 7.93 [pyr H-3]. ^{13}C NMR (CD_3CN) at −40 °C: δ 1.6 [NC*Me*]; 5.0 [Pd-*Me*]; 23.9 [*CH*$_2$]; 31.2 [*CH*$_2$]; 72.4 [N*CH*]; 118.5 [d, Ar′ *p*-C]; 125.0 [q, J(C−F) = 272.5 Hz, Ar′ CF_3]; 126.7 [pyr C-5]; 129.2 [m, Ar′ *m*-C]; 135.3 [d, Ar′ *o*-C]; 141.8 [pyr C-4]; 149.8 [pyr C-6]; 156.2 [pyr C-2]; 162.2 [q, J(B−C) = 50 Hz,Ar′ *i*-C]; 166.6 [N=*CH*]; pyr C-3 is obscured by the intense resonances from the Ar′ groups at δ 129.2. IR (Nujol, cm^{-1}): 2189 [w, ν(N≡C)]. The compound is unstable in noncoordinating solvents such as CH_2Cl_2 and $CHCl_3$.

[C_2H_4{N=CH-2-C_5H_4N(PdMe(NCCH$_3$))}$_2$][BAr′$_4$]$_2$ (6) was prepared similarly. Yield = 85%. Anal. Calcd for $C_{84}H_{50}B_2F_{48}N_6Pd_2$: C, 44.1; H, 2.2; N, 3.7. Found: C, 44.1; H, 2.2; N, 3.5. ^{1}H NMR (CD_3CN): δ 0.99 [s, 6H, Pd-Me]; 4.12 [s, 4H, CH_2]; 7.66 [m, 8H, BAr′$_4$]; 7.70 [m, 16H, BAr′$_4$]; 7.76 [br m, 2H, pyr H-5]; 7.90 [br d, 2H, pyr H-3]; 8.15 [br t, 2H, pyr H-4]; 8.52 [br s, 2H, N=CH]; 8.55 [br m, 2H, pyr H-6]; resonances due to PdNC*Me* are not observed due to exchange with the deuterated solvent. ^{13}C NMR at +25 °C (CD_3CN): δ 3.5 [br, Pd-*Me*]; 59.2 [br, N*CH*$_2$]; 118.5 [d, Ar′ *p*-C]; 125.2 [q, J(C−F) = 272.5 Hz, Ar′ CF_3]; 129.8 [m, Ar′ *m*-C]; 130.8 [br, pyr C-3] 135.3 [d, Ar′ *o*-C]; 141.9 [br, pyr C-4]; 150.9 [br, pyr C-6]; 152.0 and 157.0 [br, pyr C-2]; 162.2 [q, J(B−C) = 50 Hz, Ar′ *i*-C]; 169.0 and 176.0 [br, N=*CH*]; pyr C-5 is coincident with the larger resonances from the Ar′ groups. ^{13}C NMR at −35 °C (CD_3CN): δ 2.0−2.2 [4 × Pd-*Me*]; 57.3, 57.7, 58.3, and 58.5 [N*CH*$_2$]; 118.5 [d, Ar′ *p*-C]; 125.2 [q, J(C−F) = 272.5 Hz, Ar′ CF_3]; 129.8 [m, Ar′ *m*-C]; 123.0, 123.1 [pyr C-5]; 128.8, 129.0 [pyr C-3]; 135.3 [d, Ar′ *o*-C]; 140.8−141.0 [3 × pyr C-4]; 149.2−149.5 [4 × pyr C-6]; 150.6, 150.8, 155.2, and 155.3 [pyr C-2]; 162.2 [q, J(B−C) = 50 Hz,Ar′ *i*-C]; 167.7, 168.5, 174.2, 174.6 [N=*CH*]. IR (Nujol, cm^{-1}): 2189 [v w, ν(N≡C)].

***R,R/S,S-trans*-1,2-[C_6H_{10}{N=CH-2-C_5H_4N(PdMe(NCMe)-(COMe))}$_2$][BAr′$_4$]$_2$ (7).** CO was passed through a solution of complex **4** (0.1 g, 0.043 mmol) in CH_3CN (6 mL) for 10 min at 0 °C. Traces of a black precipitate, presumed to be Pd, were removed by filtration of the solution through Celite into a flask kept at −10 °C. The filtrate was a bright yellow color, and the solvent was removed at 0 °C under reduced pressure to give a yellow microcrystalline powder. Yield = 0.091 g (89%). Anal. Calcd for $C_{90}H_{56}B_2F_{48}N_6O_2Pd_2$: C, 45.0; H, 2.4; N, 3.5. Found: C, 44.8; H, 2.2; N, 3.1. ^{1}H NMR (CD_3CN): δ 1.39 [br m, 2H]; 1.60−2.00 [br m, 6H]; 2.6 [s, 6H, Pd-COMe]; 3.73 [br m, 2H, NCH]; 7.61−7.76 [br m, 24H, BAr_4' + 2H, pyr H-5]; 7.94 [d, 2H, pyr H-3]; 8.12 [m, 2H, pyr H-4]; 8.18 [m, 2H, pyr H-6];

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8.64 [s, 2H, N=CH]; resonances due to PdNCMe are not observed due to exchange with the deuterated solvent. ^{13}C NMR (CD_3CN) at −30 °C: δ 24.1 [CH_2]; 31.6 [CH_2]; 34.2 [PdCO*Me*]; 72.5 [NCH]; 118.5 [d, Ar′ *p*-C]; 125.2 [q, J(C−F) = 272.5 Hz, Ar′ CF_3]; 129.5 [m, Ar′ *m*-C]; 130.3 [pyr C-3]; 135.3 [d, Ar′ *o*-C]; 142.0 [pyr C-4]; 152.2 [pyr C-6]; 153.9 [pyr C-2]; 162.2 [q, J(B−C) = 50 Hz,Ar′ *i*-C]; 166.4 [N=*C*H]; 224.1 [Pd-*C*OMe]; pyr C-5 is coincident with larger resonances from the Ar′ groups at δ 125.2; the MeCN signals could not be detected. IR (Nujol, cm^{-1}): 2137 [w, ν(N≡C)], 1740 [s, ν(C=O, Pd-COMe)], 1614 [s, ν(C=N)].

[C_2H_4{(N=CH-2-C_5H_4N(PdMe(NCMe)(COMe))}$_2$]-[BAr′$_4$]$_2$ (8) was prepared similarly. ^{1}H NMR at 20 °C (CD_3CN): δ 2.49 [s, 6H, Pd−COMe]; 3.95 [s, 4H, CH_2]; 7.66 [m, 8H, BAr′$_4$]; 7.70 [m, 16H, BAr′$_4$]; 7.70 [m, 2H, pyr H-5]; 7.75 [d, 2H, pyr H-3]; 8.13 [t, 2H, pyr H-4]; 8.34 [br m, 2H, pyr H-6]; 8.42 [s, 2H, N=CH]; resonances due to PdNC*Me* are not observed due to exchange with the deuterated solvent. ^{13}C NMR (CD_3CN) at 25 °C: δ 35.0 [v br, PdCO*Me*]; 59.4 [CH_2]; 118.5 [d, Ar′ *p*-C]; 125.5 [q, J(C−F) = 272.5 Hz, Ar′ CF_3]; 129.9 [m, Ar′ *m*-C]; 135.6 [d, Ar′ *o*-C]; 141.9 [br, pyr C-4]; 151.7 [br, pyr C-6]; 152.9 [pyr C-2]; 162.2 [q, J(B−C) = 50 Hz, Ar′ *i*-C]; 170.6 [v br, N=*C*H]; pyr C-5 and C-3 are coincident with larger resonances from the Ar′ groups.

Copolymerization of Styrene and 4-Me-Styrene with CO Using Complexes 5 and 6. Styrene and 4-methylstyrene were dried over CaH_2 and distilled prior to use. In a typical polymerization reaction, complex **5** or **6** was dissolved directly in neat styrene or 4-methylstyrene to give a bright yellow solution. After 5 min, CO gas was bubbled through the solution for up to 15 h. During this period, the catalyst slowly decomposed to give a dark precipitate of Pd metal. The solution was filtered through Celite to remove Pd metal, and the Celite was washed with CH_2Cl_2. The CH_2Cl_2 solvent was removed from the combined filtrate under reduced pressure, and methanol (100 mL) was added to precipitate the polymer as a white solid, which was isolated by filtration and washed with MeOH (200 mL). The product was purified by column chromatography through silica (60 Å). The homopolymer impurity was eluted first with CH_2Cl_2, and pure copolymer was then obtained by elution with ethyl acetate. **9a**. Anal. Calcd for $(C_9H_8O)_n$: C, 81.79; H, 6.10. Found: C, 81.22; H, 6.20. ^{1}H NMR ($CDCl_3$): δ 2.60 [br d d, 1H, CH_2]; 3.10 [br m, 1H, CH_2]; 4.10 [br s, 1H, CH]; 6.60−7.45 [br m, 5H, Ph]. ^{13}C NMR ($CDCl_3$): δ 43.0−44.6 [CH_2]; 52.0−53.6 [CH]; 127.0 [Ph]; 127.8−129.4 [Ph, 2 *C*H's]; 136.6−137.5 [*ipso*-C]; 205.6−207.1 [CO]. IR (Nujol, cm^{-1}): 1710 [s, ν(C=O)]. **9b**. Anal. Calcd for $(C_{10}H_{10}O)_n$: C, 82.16; H, 6.89. Found. C, 82.50; H, 7.21. ^{1}H NMR ($CDCl_3$): δ 2.14−2.32 [br m, 3H, Me]; 2.42−4.70 [br m, 1H, CH_2]; 2.88−3.16 [br m, 1H, CH_2]; 3.90−4.08 [br m, 1H, CH]; 6.42−7.12 [br m, 4H, Ph]. ^{13}C NMR ($CDCl_3$): δ 21.0 [Me]; 43.2−44.2 [CH_2]; 52.4−53.1 [CH]; 128.0 [Ph]; 128.9−129.7 [Ph]; 133.5−134.4 [Ph]; 136.1−136.9 [Ph]; 205.7−207.4 [CO]. IR (thin film from CH_2Cl_2, cm^{-1}): 1711 [s, ν(C=O)]. **10a**. Anal. Calcd for $(C_9H_8O)_n$: C, 81.79; H, 6.10. Found: C, 81.53; H, 6.33. ^{1}H NMR ($CDCl_3$): δ 2.60 [br d d, 1H, CH_2]; 3.06 [br d d, 1H, CH_2]; 4.10 [br m, 1H, CH]; 6.55−7.40 [br m, 5H, Ph]. ^{13}C NMR ($CDCl_3$): δ 43.4 [CH_2]; 53.4 [CH]; 126.9 [Ph]; 128.2 [Ph]; 128.6−128.8 [Ph]; 136.8 [*ipso*-C]; 206.3 [CO]. IR (thin film from CH_2Cl_2, cm^{-1}): 1710 [s, ν(C=O)]. **10b**. Anal. Calcd for $(C_{10}H_{10}O)_n$: C, 82.16; H, 6.89. Found. C, 81.79; H, 6.78. ^{1}H NMR (CD_2Cl_2): δ 2.15−2.35 [m, 3H, Me]; 2.58 [br d d, 1H, CH_2]; 3.05 [br d d, 1H, CH_2]; 4.03 [m, 1H, CH]; 6.55−7.20 [br m, 4H, Ph]. ^{13}C NMR ($CDCl_3$): δ 21.0 [Me]; 43.2 [CH_2]; 53.0 [CH]; 128.4 [Ph]; 129.4−130.0 [Ph]; 134.4 [br, Ph]; 137.2 [br m, Ph]; 206.9 [CO]. IR (thin film from CH_2Cl_2, cm^{-1}): 1710 [s, ν(C=O)]. The optically active copolymers **9a*** and **9b*** were prepared similarly using the chiral nonracemic complex *R,R-trans*-1,2-[C_6H_{10}{N=CH-2-C_5H_4N(PdMe$_2$)}$_2$], **3***.

X-ray Crystal Structure Determination of 3. Crystals of complex *R,R*/*S,S*-**3**·CH_2Cl_2 were grown by slow evaporation of a concentrated methylene chloride solution. An orange crystal was mounted on a glass fiber. Data were collected using a Nonius Kappa-CCD diffractometer using COLLECT (Nonius, 1998) software. Crystal cell refinement and data reduction were carried out using the Nonius DENZO package. The data were scaled using SCALEPACK (Nonius, 1998). Crystallographic details are given in Table 2. The SHELXTL 5.1 (Sheldrick, G. M., Madison, WI) program package was used to solve the structure by direct methods, followed by successive difference Fouriers. All non-hydrogen atoms were refined anisotropically. The solvent was also modeled anisotropically but without hydrogen atoms. The hydrogen atoms were calculated geometrically and were riding on their respective carbon atoms.

Table 2. Crystallographic Details for Complex 3

formula, fw	$C_{23}H_{32}Cl_2N_4Pd_2$, 648.23
temp, K	150(2)
wavelength, Å	0.71073
cryst syst	orthorhombic
space group	*Pccn*
a	11.6000(3)
b	12.0609(3)
c	18.2409(5)
V, Å^3; *Z*	2552.02(12); 4
d(calcd), Mg/m^3	1.687
abs coeff, mm^{-1}	1.636
F(000)	1296
cryst size, mm^3	0.28 × 0.13 × 0.08
θ range, deg	2.68 to 27.49
no. of rflns collected	36 060
no. of indep rflns	2930 [*R*(int) = 0.060]
max./min. transmn	0.8871/0.6618
no. of data/restraints/params	2930/0/141
goodness of fit on F^2	1.066
final *R* indices [$I>2\sigma(I)$]	R1 = 0.0377, wR2 = 0.1134
R indices (all data)	R1 = 0.0613, wR2 = 0.1218
largest diff peak and hole, e Å^{-3}	1.143 and −1.023

Acknowledgment. We thank NSERC (Canada) for financial support and for a graduate scholarship for C.R.B. We also thank Dr. C. W. Kirby for his help in performing NOESY and ROESY experiments.

Supporting Information Available: Tables of X-ray data for complex **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0102706