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C-Substituted Bis(diphenylphosphino)methane-Type Ligands for Chromium-Catalyzed Selective Ethylene Oligomerization Reactions

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Summary: Ligand backbone alkylation of the complex $[Cr(CO)_4(dppm)]$ *(dppm = bis(diphenylphosphino)methane) with alkyl iodides yields the C-substituted dppm ligand complexes* $[Cr(CO)_4\{Ph_2PCH(R)PPh_2\}]$ *(R = methyl, n-hexyl, benzyl). Activation of these complexes via one-electron oxidation with* $Ag[(Al(OC_4F_9)_4]$ *and CO removal with triethylaluminium, or (in the case of R = methyl) by in situ treatment of the free ligand with a chromium salt and modified methyl alumoxane (MMAO), leads to catalysts showing some selectivity for ethylene trimerization and tetramerization. NMR spectroscopic studies of the parent dppm or* $[Cr(CO)_4(dppm)]$ *compounds suggest that ligand deprotonation and decomplexation may be the cause of the surprisingly poor catalytic performance of these specific derivatives.*

Introduction

In recent years, catalysts have emerged that are capable of the selective trimerization of ethene to 1-hexene via a distinctive metallacyclic mechanism.[1] In 2002, we reported catalysts based on chromium complexes of ligands of the type $Ar_2PN(Me)PAr_2$ (Ar = *ortho*-methoxy-substituted aryl group) with productivity figures over an order of magnitude better than previous systems.[2] This unprecedented performance led to interest both from a mechanistic viewpoint and in extending the range of substrates used in these reactions;[3] however, the most significant subsequent development has been the report from Bollmann and co-workers that demonstrated that relatively minor changes to ligand structure and reaction conditions can lead to ethene tetramerization rather than trimerization.[4] More recently, a wider variety of carbon-bridged diphosphine ligands has been investigated for these reactions, with 1,2-bis(diphenylphosphino)benzene, in particular, showing promise.[5] Surprisingly, bis(diphenylphosphino)methane ligands, despite being very similar to the highly active and selective *N,N*-bis(diphenylphosphino)amine in terms of bite angle, steric constraints, and donor strength,[6] proved to be very poor ligands for catalysis. Indeed, the direct analogue dppm showed no evidence of selective oligomerization, producing only a Schulz−Flory distribution of oligomers.[5] This result is in line with our earlier findings for *P*-anisyl-substituted derivatives.[2] It was postulated that the unsubstituted nature of the backbone made the ligand susceptible to deprotonation during catalysis, leading to the observed disappointing results. With this hypotheses in mind, and to access ligands sterically equivalent to the successful *N*-alkyl-substituted *N,N*-bis(diphenylphosphino)amines, it was reasoned that ligands of the type $Ph_2PCH(R)PPh_2$ (R = alkyl) may give improved performance. The synthesis and catalytic screening of such complexes are reported here.

Results and Discussion

Shaw and co-workers reported the synthesis of backbone-substituted dppm ligands via deprotonation and alkylation of various simple dppm complexes, in which complexation acts to protect phosphorus from substitution.[7] Of particular interest for this study is the report of chromium carbonyl complexes, such species being useful precatalysts that can be activated via one-electron oxidation.[8] Following Shaw's method, complexes **2**−**4** were synthesized in 38−63% yield from $[Cr(CO_4)(dppm)]$ **1** (Scheme 1). IR spectroscopy reveals the carbonyl stretching bands for these complexes to be very similar (1877, 1894, 1917, 2007 cm^{-1} for **2**, 1876, 1892,

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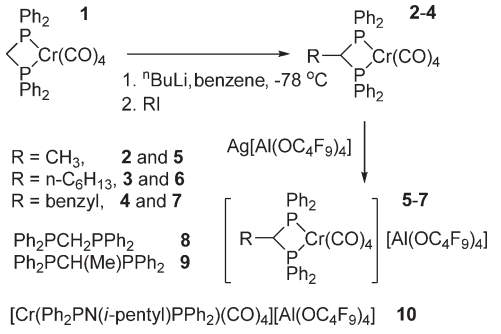
Scheme 1. Synthesis of Complexes



1917, 2005 cm^{-1} for **3**, and 1877, 1894, 1918, 2006 cm^{-1} for **4**) and close to the values for the related *N,N*-bis-(diphenylphosphino)amine complexes[8] (for $[Cr(CO)_4(Ar_2PN(Me)PAr_2)]$, Ar = 2-$C_6H_4$(MeO), 1869, 1888, 1907, 2002 cm^{-1}). This suggests the effect of the less electronegative carbon backbone is offset by the potential for delocalization of the lone pair into the P−N−P chelate. It also suggests on simple electronic grounds these ligands may be expected to have similar performance in catalysis. Crystals of compound **2**, suitable for X-ray diffraction study, were obtained by dichloromethane at −30 °C; the structure is illustrated in Figure 1.

Compound **2** shows the expected octahedral coordination at chromium with a nonplanar Cr−P−C−P ring (deviation of C25 from planarity = 0.513 Å) with a methyl substituent pseudoequatorial on the carbon backbone. The P−Cr−P bite angle is 70.58(2)°, very similar to the related $[Cr(CO)_4(Ar_2PCH_2PAr_2)]$, Ar = 2-$C_6H_4$(MeO), with an angle of 71.52(5)° and the trimerization-active precatalyst $[Cr(CO)_4(Ar_2PN(Me)PAr_2)]$ with an angle of 68.44(3)°.[8b] The Cr−C bond lengths for the CO ligands trans to the diphosphine are 1.846(3) Å for C(28) and 1.850(3) Å for C(30) and are slightly shorter than the other Cr−C bonds at 1.880(3) Å for C(27) and 1.877(3) Å.

Treatment of **5**−**7** with $Ag[Al(OC_4F_9)_4]$ leads to smooth one-electron oxidation and generates complexes **5**−**7** with carbonyl stretching bands shifted to higher wavenumber (for example 1966, 2011, 2043, and 2088 cm^{-1} for **5**) as expected. Cyclic voltammetry of **2**−**4** reveals reversible oxidation in each case with $E_{1/2}$ of 0.68, 0.69, and 0.79 V vs SCE, respectively. Complexes **5**−**7** may be activated using triethylaluminum as a CO scavenger;[7] oligomerization results are presented in Table 1.

Complexes **5**−**7** all exhibit modest activity and some selectivity to C_6 and C_8 products above that expected for a Schulz−Flory distribution. Unfortunately, significant amounts of polymeric product are also observed, especially in runs 1 and 3. Increasing the chain length of the ligand C-substituent from methyl to *n*-hexyl approximately doubles activity and significantly reduces the amount of polymer byproduct; a modest increase in the selectivity to octene over hexane is also observed. The benzyl derivative retains much of this activity but has extremely poor selectivity: it is noteworthy that *N,N*-bis(diphenylphosphino)benzylamine ligands also have poor performance. For comparison complex **10** was prepared and tested; this variant with the P−N−P ligand framework showed the activity and productivity associated with the amine backbone ligand, the selectivity toward tetramerization being as expected, with a low polymer formation level.

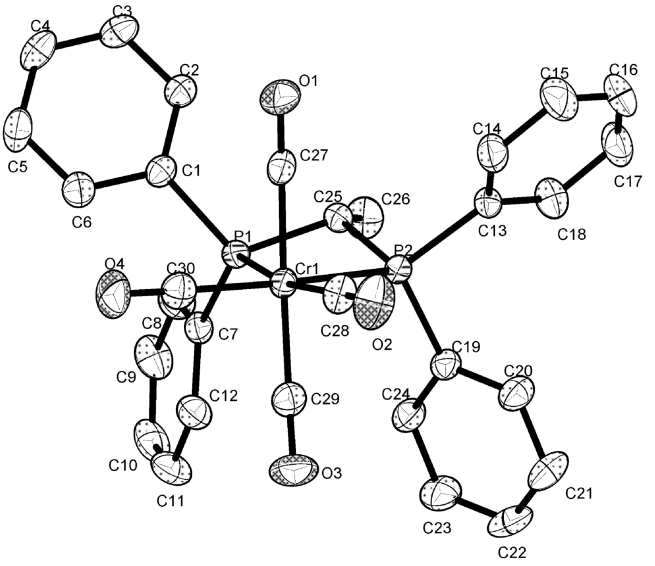


Figure 1. Molecular structure and numbering scheme for **2**. All hydrogen atoms are omitted for clarity; thermal ellipsoids are set to 50% probability. Selected bond lengths (Å) and angles (deg): Cr(1)−C(28) 1.846(3), Cr(1)−C(30) 1.850(3), Cr(1)−C(29) 1.877(3), Cr(1)−C(27) 1.880(3), Cr(1)−P(2) 2.3535(7), Cr(1)−P(1) 2.3593(7), P(1)−C(1) 1.813(2), P(1)−C(7) 1.815(3), P(1)−C(25) 1.852(2), P(2)−C(19) 1.817(2), P(2)−C(13) 1.819(2), P(2)−C(25) 1.852(2), C(27)−O(1) 1.144(3), C(28)−O(2) 1.149(3), C(29)−O(3) 1.143(3), C(30)−O(4) 1.152(3), P(2)−Cr-(1)−P(1) 70.58(2), P(2)−C(25)−P(1) 94.62(11).

The activation method of choice has previously been shown to have a profound effect on oligomerization activity and selectivity, and to benchmark our results against previous studies, which often rely on *in situ* activation of a chromium salt and ligand with MAO or MMAO,[1−5] we synthesized the free methyl-substituted ligand **9** using the recent method of Hogarth and co-workers.[9] Screening of this ligand with $[Cr(acac)_3]$ and MMAO gave an approximate order of magnitude increase in productivity and a reduction in polymer levels compared to the previous activation route. Comparison of these new ligands with dppm shows that backbone substitution leads to an increase in productivity in every case; selectivity is also influenced with dppm giving what is best described as a Schulz−Flory distribution (α = 0.55).[5] It has been previously reported that attempts to prepare the complex $[Cr(dppm)(CO)_4][Al(OC_4F_9)_4]$ were met with decomposition;[8a] thus no direct comparison of the catalysis with complexes **5**−**7** can be made with the dppm analogue. Clearly, our approach has led to an improvement in catalysis results, although it is sobering to compare these results to the *N,N*-bis(diphenylphosphino)isopentylamine ligand complex **10**, which gives higher activity and significantly better selectivity.

In an attempt to understand the poor performance of dppm and the possibility of ligand deprotonation during catalysis, an NMR-scale reaction in which dppm was treated with 300 equiv of MMAO in toluene was performed. The ligand is remarkable robust in the presence of this cocatalyst, the ^{31}P NMR resonance at δ −22.6 remaining the only signal at room temperature for 30 min. Repeating this experiment at the catalytic reaction temperature of 60 °C still only leads

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Table 1. Ethylene Oligomerization Results

run[a]	catalyst	activity (g/g Cr/h)	productivity (g/g Cr)	polymer (wt %)	oligomers/wt % of liquid fraction[b]					
					C_4	C_6 (1 − C_6)	C_8 (1 − C_8)	C_{10}	C_{12}	C_{14}
1	**5**	44 080	8130	53.7	6.5	23.9 (70.4)	34.6 (91.3)	5.3	4.0	3.4
2	**6**	82 820	23 010	17.0	3.8	18.8 (48.0)	38.4 (95.2)	6.5	5.4	4.6
3	**7**	70 150	19 490	64.3	5.3	21.9 (50.0)	30.8 (91.3)	7.8	6.3	5.3
4	**10**	1 920 775	733 096	0.9	1.8	28.8 (81.6)	63.0 (99.4)		5.4[e]	
5[c]	**9**	790 180	219 490	29.6	3.7	16.2 (49.8)	34.1 (95.9)	6.5	6.1	5.3
6[d]	**8**	21 000			Schulz−Flory distribution of LAOs (α = 0.55)					

[a] Conditions unless stated otherwise: 2.5 μmol of compound, 150 equiv of triethylaluminium, chlorobenzene diluent, 55 bar of ethene, 60 °C. [b] Determined by GC; remainder is C_{16-20+}. [c] Conditions as run 1 except **9** added to [Cr(acac)$_3$] (2.5 μmol), then MMAO (960 equiv) added. [d] Taken from ref 5. [e] Total C_{10-14}.

to slow decomposition (30% decomposition after 30 min) to a species with a ^{31}P NMR resonance at δ −7.1. These NMR data are consistent with previously reported alkyl aluminum bis(diphenylphosphino)methide compounds,[10] the expected ligand deprotonation products, but the slow rate of formation at this temperature is surprising. Clearly, coordination of the ligand to a metal center will influence this reactivity, but observation of such species is frustrated by the paramagnetism of the Cr(I) or Cr(III) precatalysts. As a model reaction, treatment of [Cr(CO)$_4$(dppm)] with 300 equiv of MAO in toluene was carried out. Again, the ligand of the complex is remarkably robust, and only after 30 min at 60 °C is any decomposition observed, interestingly to the same species at δ −7.1, suggesting ligand decomplexation. These studies, although not conclusive, point to deprotonation under catalytic conditions being surprisingly difficult; a simple steric influence from backbone substitution may be a better explanation for the improved performance of these new catalysts.

Conclusions

We have synthesized new ethene trimerization- and tetramerization-active catalysts based on chromium complexes of C-substituted dppm ligands. Our synthetic route can be thought of as a particularly efficient protecting group strategy in which potentially reactive phosphorus(III) centers are protected by complexation to the oligomerization-active metal, chromium. Performance is enhanced compared to unsubstituted dppm catalysts, tentatively attributed to increased stability against deprotonation and decomplexation during catalysis, but still falls well short of the outstanding performance demonstrated by *N,N*-bis(diarylphosphino)-amine catalysts.

Experimental Section

General Procedures. All procedures were carried out under an inert (N_2) atmosphere using standard Schlenk line techniques or in an inert atmosphere (Ar) glovebox. Chemicals were obtained from Sigma Aldrich or Fisher Scientific and used without further purification unless otherwise stated. Modified methyl aluminoxane (MMAO) was obtained from Akzo-Nobel as a 7 wt % solution in hexane. All solvents were purified using an Anhydrous Engineering Grubbs-type solvent system. Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrometer in dichloromethane. NMR spectra were recorded on a JEOL ECP 300 spectrometer at 300 MHz (^{1}H) and 121 MHz (^{31}P{^{1}H}), a JEOL delta 400 at 200.6 MHz (^{13}C{^{1}H}), and a JEOL lambda 300 at 282 MHz (^{19}F), in deuterated solvent. ^{1}H and ^{13}C{^{1}H} NMR spectra are referenced with chemical shifts relative to high frequency of residual solvent, ^{31}P NMR spectra are referenced relative to high frequency of 85% H_3PO_4 and ^{19}F NMR spectra are referenced relative to high frequency of CCl_3F. Mass spectrometry was carried out by the Mass Spectrometry Service at the School of Chemistry at the University of Bristol. Microanalyses were carried out by the Microanalytical Laboratory of the School of Chemistry at the University of Bristol. Complex **10** was synthesized in an analogous method to that previously reported.[8a]

Synthesis of 2−4. The same general method was followed in each case and is described here for **2**.

[Cr(CO)$_4$(dppm)] (0.50 g; 0.91 mmol) and *N,N,N′,N′*-tetramethylethylenediamine (0.21 mL; 1.37 mmol) were stirred in benzene (20 mL), giving a clear yellow solution. To this stirred solution was added dropwise ^{n}BuLi (1.6 M in hexanes; 0.86 mL; 1.37 mmol) at ambient temperature. After 1 h, methyl iodide (0.11 mL; 1.82 mmol) was added and the solution was stirred for 4 h at 60 °C. On cooling, degassed water (20 mL) was added and the solution stirred, then left to separate. The organic layer was collected and dried ($MgSO_4$) and the solvent removed *in vacuo* to give a yellow solid (0.21 g; 0.37 mmol; 41%). Crystals suitable for X-ray diffraction study were obtained from a concentrated dichloromethane solution cooled to −30 °C.

Characterizing data for 2: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.11−1.24 (td, 3H, J_{P-H} = 13.8 Hz, J_{H-H} = 7.8 Hz, C$\underline{H}_3$), 4.75 (m, 1H, C$\underline{H}$), 7.33 − 7.60 (m, 20H, Ar$\underline{H}$); ^{31}P NMR ($CDCl_3$) δ 46.95; ^{13}C NMR ($CDCl_3$) δ 15.57 (s, $\underline{C}H_3$), 53.94 (t, J_{CP} = 16.4 Hz, *C*H), 128.48 (d, J_{CP} = 4.6 Hz), 128.85, 130.14, 130.52 (s, *C*H), 131.33 (t, J_{CP} = 5.7 Hz, *C*H), 134.14 (t, J_{CP} = 6.7 Hz, *C*P); IR (CH_2Cl_2) ν 1877 (C≡O), 1894 (C≡O), 1917 (C≡O), 2007 (C≡O) cm^{-1}; MS (ESI, CH_2Cl_2) *m*/*z* 562.0 (M^+). Anal. Calcd for $C_{30}H_{24}CrO_4P_2$: C 64.06, H 4.30. Found: C 63.98, H 4.84. $E_{1/2}$: 0.68 V vs SCE.

Characterizing data for 3: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.76 (t, 3H, *J* = 6.99 Hz, C$\underline{H}_3$), 0.96 (m, 4H, C$\underline{H}_2$C$\underline{H}_2$CH$_3$), 1.10 (m, 4H, CH(CH$_2$C$\underline{H}_2$C$\underline{H}_2$-CH$_2$CH$_2$CH$_3$)), 1.51 (dt, 2H, *J* = 6.48, 21.36 Hz, CH(C$\underline{H}_2$)), 4.60 (m, 1H, C$\underline{H}$(*n*-hexyl)), 7.33−7.58 (m, 20H, Ar*H*) ; ^{31}P NMR ($CDCl_3$) δ 48.84; ^{13}C NMR ($CDCl_3$) δ 1.12 (s, *C*H$_3$), 14.01, 22.46, 28.82, 29.35, 31.34 (s, *C*H$_2$), 60.31 (t, J_{CP} = 16.5 Hz *C*H), 128.65 (d, J_{CP} = 21.3 Hz, *C*H), 130.06, 130.52, 131.36, (s, *C*H) 132.81 (t, J_{CP} = 11 Hz *C*H), 134.08 (s, *C*P); IR (CH_2Cl_2) ν 1876 (C≡O), 1892 (C≡O), 1917 (C≡O), 2005 (C≡O) cm^{-1}; MS (ESI, CH_2Cl_2) *m*/*z* 632.0 (M^+). Anal. Calcd for $C_{35}H_{34}CrO_4P_2$: C 66.45, H 5.42. Found: C 66.56, H 4.87. $E_{1/2}$: 0.69 V vs SCE.

Characterizing data for 4: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.87 (m, 2H, C$\underline{H}_2$), 4.96 (m, 1H, C$\underline{H}$), 6.60 (m, 2H, *o*-Bz$\underline{H}$), 7.12 (m, 3H, *m*/*p*-Bz$\underline{H}$), 7.29−7.55 (m, 20H, Ar$\underline{H}$); ^{31}P NMR ($CDCl_3$) δ 51.62; ^{13}C NMR ($CDCl_3$) δ 36.00 (s, $\underline{C}H_2$), 61.98 (t, J_{CP} = 12.7 Hz, *C*H), 126.91, 128.44, 128.48, 128.53, 128.57, 128.68 (s, Bz *C*H), 128.75 (d, J_{CP} = 4.6 Hz, *C*H), 128.83 (d, J_{CP} = 4.6 Hz, *C*H),

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130.10, 130.60 (s, *C*H), 131.78 (t, J_{CP} = 6.1 Hz, *C*H), 134.19, (d, J_{CP} = 12.1 Hz, *C*P); IR (CH_2Cl_2) ν 1877 (C≡O), 1894 (C≡O), 1918 (C≡O), 2006 (C≡O) cm^{-1}; MS (ESI, CH_2Cl_2) m/z 638.0 (M^+). Anal. Calcd for $C_{36}H_{28}CrO_4P_2$: C 67.71, H 4.42. Found: C 67.70, H 4.62. $E_{1/2}$: 0.79 V vs SCE.

Synthesis of 5−7. The same general method was followed in each case and is described here for **5**.

A Schlenk flask was charged with **2** (0.12 g, 0.213 mmol), and dichloromethane (15 mL) was added. $Ag[Al(OC_4F_9)_4]$ (0.23 g, 0.213 mmol) was added to the solution, and an immediate color change to deep purple was observed. The mixture was stirred at ambient temperature for 1 h, after which a second equivalent of $Ag[Al(OC_4F_9)_4]$ was added and the mixture stirred overnight. The solution was then filtered, and the solvent was removed *in vacuo*. The resultant purple solid was washed with hexane (2 × 10 mL) and dried *in vacuo* (0.26 g; 0.170 mmol; 79.8%).

Characterizing Data for 5: ^{19}F NMR ($CDCl_3$, 282 MHz) δ −75.2 (s, $\nu_{1/2}$ = 16.5 Hz); IR (CH_2Cl_2) ν = 1966 (C≡O), 2011 (C≡O), 2043 (C≡O), 2088 (C≡O) cm^{-1}; MS (ESI nanospray, positive and negative mode, CH_2Cl_2) m/z 562.0 (M^+), 966.9 (A^-); trace amounts of residual silver salts meant that satisfactory elemental analysis could not be obtained.

Characterizing data for 6: ^{19}F NMR ($CDCl_3$, 282 MHz) δ −75.2 (s, $\nu_{1/2}$ = 15.5 Hz); IR (CH_2Cl_2) ν 1964 (C≡O), 2010 (C≡O), 2043 (C≡O), 2088 (C≡O) cm^{-1}; MS (ESI nanospray, positive and negative mode, CH_2Cl_2) m/z 632.0 (M^+), 966.9 (A^-). Anal. Calcd for $C_{51}H_{34}AlCrF_{36}O_8P_2$: C 38.29, H 2.14. Found: C 38.22, H 2.85.

Characterizing data for 7: ^{19}F NMR ($CDCl_3$ 282 MHz) δ −75.2 (s, $\nu_{1/2}$ = 17.1 Hz); IR (CH_2Cl_2) ν 1966 (C≡O), 2011 (C≡O), 2043 (C≡O), 2089 (C≡O) cm^{-1}; MS (ESI nanospray, positive and negative mode, CH_2Cl_2) m/z 638.0 (M^+), 966.8 (A^-); trace amounts of residual silver salts meant that satisfactory elemental analysis could not be obtained.

Crystallographic Details. A single crystal of **2** was mounted in inert oil and transferred to the cold gas stream of the diffractometer. X-ray measurements were made for **2** using a Bruker SMART CCD three-circle diffractometer with Mo K_α radiation (λ = 0.71073 Å). The hydrogen atom on C25 was located in the electron density difference map and refined isotropically, whereas all others were assigned ideal geometries. Crystal data for **2**: $C_{30}H_{24}CrO_4P_2$, M = 562.43, orthorhombic space group *Pbca*, a = 15.8426(9) Å, b = 16.7783(10) Å, c = 20.2915(12) Å, U = 5393.7(5) $Å^3$, T = 173(2) K, Z = 8, μ(Mo K_α) = 1.385 mm^{-1}, 55 001 reflections measured, 6227 unique (R_{int} = 0.0932), which were used in all calculations. The final R_1 [$I > 2\sigma(I)$] was 0.0453.

Ethene Oligomerization Runs. Ethene oligomerization was carried out in a 300 mL stainless steel reactor with mechanical stirring. The oven-dried vessel was purged with N_2 followed by ethene, charged with diluent (90 mL), and heated to the required run temperature. The catalyst solution was prepared by dissolving the required amount of catalyst in diluent (10 mL) and adding the required amount of trialkylaluminum (AlR_3) or MMAO. The solution was injected into the prepared autoclave, and the reactor was immediately charged with the required pressue of ethene and maintained at this pressure for the duration of the reaction. After the run time, the reactor was cooled in an ice bath, the excess ethene was bled, and an internal standard was added (nonane, 1000 μL). After quenching with MeOH followed by 10% HCl, the organic phase was analyzed by GC, and the white solids were filtered, washed, dried, and weighed.

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Supporting Information Available: Crystallographic data as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.