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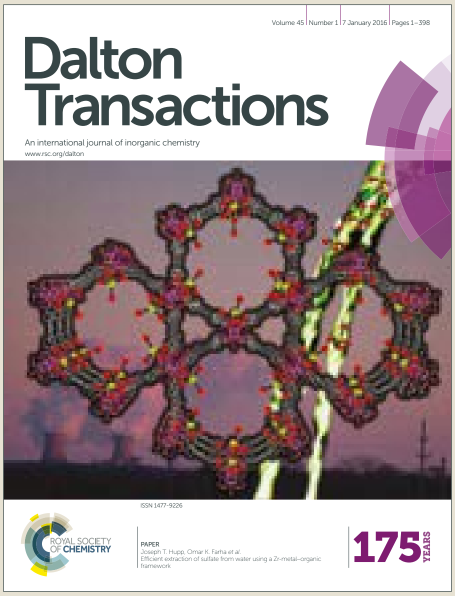

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ARTICLE

First-row early transition metal complexes with a highly sterically demanding triisopropylphenyl amino triphenolate ligand: synthesis and applications

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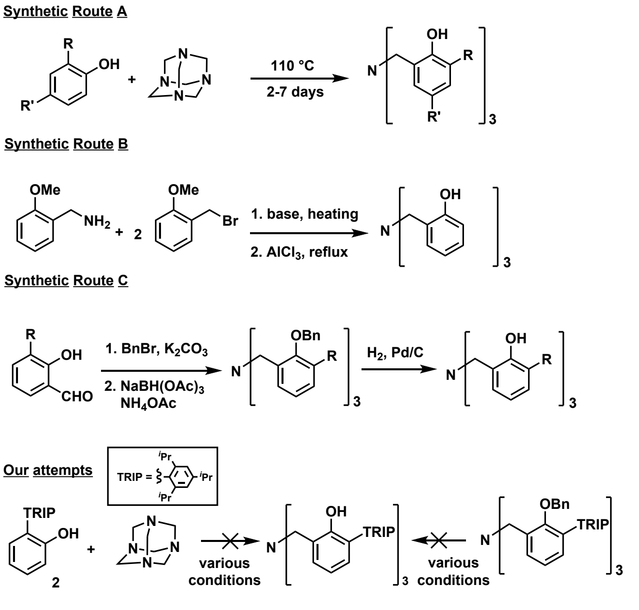
Amino triphenolate ligands have been widely used for the synthesis of various transition metal complexes aiming at various applications such as ring-opening polymerization, olefin polymerization, and sulfoxidation. However, the introduction of highly sterically demanding aromatic substituents, such as triisopropylphenyl (TRIP), to the amino triphenolate ligand has not been previously reported probably due to the synthetic difficulty. In six-step reactions using commercial materials, a highly sterically demanding amino triphenolate ligand was successfully synthesized, and early transition metal complexes (Ti, V, Cr, Mn) supported by the ligand were also obtained and fully characterized. In addition, titanium and chromium complexes were further used for catalytic sulfoxidation, and polymerization of ethylene, respectively.

Introduction

Ligands in transition metal chemistry control the environment of the metal and are thus key players in a variety of catalytic reactions.[1] Therefore, tremendous efforts have been made to modulate the electronic and steric properties of the coordination geometry of metal centers. Multidentate ligands have been widely investigated for securing robustness and stability to transition metal catalysts. Among various multidentate ligands, amino triphenolate ligands have recently emerged as new candidates for transition metal catalysts. For example, the metal complexes supported by amino triphenolates were successfully used for various applications, such as ring-opening polymerization (ROP),[2] olefin polymerization,[3] and sulfoxidation.[4] Therefore, in the last two decades, a variety of their complexes have been synthesized and applied to a wide variety of transition metals[3e, 4c, 5] and main group elements.[6]

Although there are various precedents to sterically demanding amino triphenolates, amino triphenolate ligands decorated by highly substituted aromatic groups have less studied. At first glance, the synthesis of amino triphenolate substituted by functionalized aromatic groups seems facile because several synthetic routes have been reported (Scheme 1). However, such known precedents were not effective with a highly bulky aromatic group, such as triisopropylphenyl (TRIP). Synthetic routes A and C were applied to access a highly sterically demanding triisopropylphenyl amino triphenolate (TRIP-ATP) ligand under various conditions,[7] but all attempts were unsuccessful. Therefore, we set out to develop a new synthetic method to prepare TRIP-ATP. Herein, we report its synthesis and early transition metal complexes, and applications of the titanium and chromium complexes. The key to the successful preparation of the bulky ligand was to use an allyl protection group, which did not affect the subsequent deprotection step.



Scheme 1. Synthetic approaches to the amino triphenolate ligand, and our attempts to introduce triisopropylphenyl (TRIP) to amino triphenolate.

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We investigated the complexation of TRIP-ATP with first-row early transition metals because early transition metals typically have a strong affinity toward phenolate ligands. Early transition metal or oxophilic metal complexes have been applied to various reactions including amination,[8] olefin polymerization,[9] cyclic esters/carbonates ROP[2d, 10] and ketone hydrosilylation.[11] Thus, we also explored their catalytic activities for these reactions. A titanium complex with TRIP-ATP was found to be efficient for selective sulfoxidation of thioanisoles. A chromium complex with TRIP-ATP was found to be efficient for the preparation of high density polyethylene (HDPE) with a high melting point, which may have resulted from the highly steric effect of the ligand.

Experimental Section

The synthesis of the ligand precursors (**1**-**5**), density functional theory (DFT) calculations for vanadium and chromium complexes, and details of sulfoxidation and ethylene polymerization are described in the Supplementary Information.

Tris{[2-(hydroxy)-2',4',6'-triisopropyl-3-biphenylyl]methyl}amine (6). K_2CO_3 (3.63 g, 26.2 mmol, 3.0 equiv.), $Pd(PPh_3)_4$ (0.707 g, 0.07 equiv.) and **5** (9.29 g, 8.74 mmol, 1.0 equiv.) were added to a 350-mL heavy wall round-bottom flask. Dry tetrahydrofuran (THF; 90 mL) and methanol (60 mL) were added to the flask. The resulting mixture was stirred in the sealed flask at 50 °C for 24 h. Distilled water was then added to the flask and the organic layer was extracted with pentane (4 × 30 mL). The combined organic layers were filtered through a pad of Celite. The layers were then filtered through a pad of silica. The combined organic layers were dried to afford **6** as a colorless solid (6.43 g, 78 %). ^1H NMR (500 MHz, $CDCl_3$, 23 °C, δ): 7.22 (dd, J = 7.7, 1.6 Hz, 3H), 7.06 (s, 6H), 6.94 (dd, J = 7.5, 1.6 Hz, 3H), 6.85 (t, J = 7.6 Hz, 3H), 6.68 (s, 3H), 3.84 (s, 6H), 2.93 (sept, J = 6.9 Hz, 3H), 2.56 (sept, J = 6.8 Hz, 6H), 1.30 (d, J = 6.6 Hz, 18H), 1.01 (dd, J = 6.9, 5.1 Hz, 36H). ^{13}C NMR (125 MHz, CDCl3, 23 °C, δ): 153.2, 148.9, 148.1, 130.7, 130.2, 129.9, 126.6, 122.8, 121.3, 119.5, 53.9, 34.5, 30.6, 24.6, 24.2, 24.0. Anal. Calcd. for $C_{66}H_{87}NO_3$: C, 83.77; H, 9.63; N, 1.21; found: C, 84.12; H, 9.31; N, 1.49.

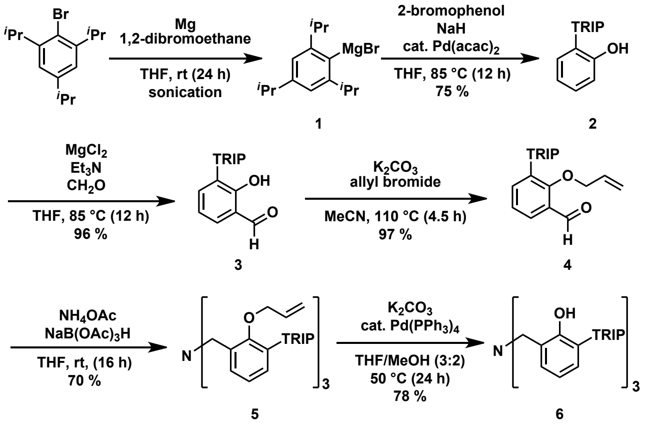
6-Ti. 6 (100.0 mg, 0.106 mmol, 1.0 equiv.) was added to a 20 mL vial followed by addition of 6 mL of dry benzene. $Ti(O^iPr)_4$ (35.3 μL, 0.117 mmol, 1.1 equiv.) was added to the vial. The mixture was stirred at 23°C for 12 h. The solution was filtered through a pad of Celite and volatiles were removed *in vacuo* to obtain **6-Ti** as a colorless solid (94.1 mg, 85 %). X-ray quality single crystals were grown by vapor diffusion (C_6H_6/pentane) at –40 °C over several days. ^1H NMR (500 MHz, C_6D_6, 23 °C, δ): 7.16 (s, 3H), 7.14–7.12 (m, 6H) 6.94 (d, J = 1.50 Hz, 1H), 6.92 (d, J = 1.53 Hz, 2H), 6.88 (t, J = 7.40 Hz, 3H) 4.16 (d, J = 13.76 Hz, 3H), 3.98 (sept, J = 6.18 Hz, 1H), 2.91–2.80 (m, 6H), 2.66 (d, J = 13.9 Hz, 3H), 2.55 (sept, J = 6.83 Hz, 3H), 1.34 (d, J = 6.70 Hz, 9H), 1.27 (d, J = 6.97 Hz, 9H), 1.26 (d, J = 6.97 Hz, 9H), 1.24 (d, J = 6.83 Hz, 9H), 1.08 (d, J = 6.83 Hz, 9H), 1.07 (d, J = 6.97 Hz, 9H), 0.58 (d, J = 6.18 Hz, 3H), 0.54 (d, J = 6.18 Hz, 3H). ^{13}C NMR (125 MHz, C_6D_6, 23 °C, δ): 161.0, 148.1, 147.2, 147.2, 133.6, 131.4, 124.6, 120.6, 120.4, 120.4, 80.4, 58.1, 34.9, 31.2, 31.1, 25.5, 24.7, 24.6, 24.5, 24.4, 24.4, 24.3. Anal. Calcd. for $C_{69}H_{91}TiNO_4{\cdot}(H_2O)_{1.3}$: C, 77.47; H, 8.82; N, 1.31; found: C, 77.37; H, 8.74; N, 1.32. IR (KBr, cm^{-1}): 3054 (s (br), C–H), 2958 (s, C–H), 2927 (s, C–H), 2866 (s, C–H), 1445 (s), 1433 (s), 1241(s), 1011(m), 874 (s), 709 (m), 858 (m).

6-V. Et_3N (89.0 μL, 6.0 equiv.) and **6** (100.0 mg, 0.106 mmol, 1.0 equiv.) were added to a 20 mL vial. Dry toluene (10 mL) was added to the vial. The mixture was stirred at 23°C for 30 min. $VCl_3(THF)_3$ (39.6 mg, 0.106 mmol, 1.0 equiv.) was then added to the vial. The resulting mixture was stirred at 60 °C for 12 h. The solvents were removed *in vacuo*. The solid residue was extracted with pentane (4 x 3 mL). The mixture was filtered through a pad of Celite, and dried *in vacuo* to afford **6-V** as a yellow solid (93.2 mg, 83 %). X-ray quality single crystals were grown from a saturated pentane solution at –40 °C over several days. Anal. Calcd. For $C_{70}H_{92}VNO_4{\cdot}(\text{pentane})_{1.2}$: C, 79.44; H, 9.33; N, 1.22; found: C, 79.98; H, 8.83; N, 1.44. Solution magnetic moment (C_6D_6): 2.66 μ_B. IR (KBr, cm^{-1}): 2958 (s, C–H), 2930 (s, C–H), 2868 (s, C–H), 1594 (m), 1430 (m), 1360 (s), 1243 (m), 1070(m), 861 (m), 756 (s).

6-Cr. NaH (7.9 mg, 3.1 equiv.) and **6** (100.0 mg, 0.106 mmol, 1.0 equiv.) were added to a 20 mL vial. Dry THF (10 mL) was added to the vial. The resulting mixture was stirred at 23 °C for 30 min. $CrCl_3(THF)_3$ (39.8 mg, 0.106 mmol, 1.0 equiv.) was then added to the vial. The mixture was stirred at 60 °C for 24 h. The solvents were removed *in vacuo*. The solid residue was extracted with pentane (4 x 3 mL). The extracted solution was removed *in vacuo* to afford **6-Cr** as a green solid (75.6 mg, 67 %). X-ray quality single crystals were grown from a saturated pentane solution at –40 °C over several days. Anal. Calcd. For $C_{70}H_{92}CrNO_4{\cdot}H_2O$: C, 77.74; H, 8.76; N, 1.30; found: C, 77.42; H, 8.86; N, 1.31. Solution magnetic moment (C_6D_6): 3.76 μ_B. IR (KBr, cm^{-1}): 2958 (s (br), C–H), 2927 (s, C–H), 2868 (s, C–H), 1589 (s), 1430 (m), 1360 (s), 1274(m), 1043(m), 859 (s), 752 (s).

6-Mn. NaH (7.9 mg, 0.329 mmol, 3.1 equiv.) and **6** (100.0 mg, 0.106 mmol, 1.0 equiv.) were added to a 20 mL vial. Dry THF (10 mL) was added to the vial. The resulting mixture was stirred at 23 °C for 30 min. $Mn(acac)_3$ (37.4 mg, 0.106 mmol, 1.0 equiv.) was then added to the vial and the resulting mixture was stirred at 60 °C for 12 h. The solvent was removed *in vacuo*. The solid residue was extracted with diethyl ether (4 x 3 mL). The mixture was filtered through a pad of Celite, and dried *in vacuo* to afford **6-Mn** as a green solid (33.8 mg, 26 %). X-ray quality single crystals were grown from a saturated diethyl ether solution at –40 °C over several days. Anal. Calcd. For $C_{75}H_{99}MnNNa_2O_6{\cdot}(H_2O)_{0.6}$: C, 73.70; H, 8.26; N, 1.15; found: C, 73.33; H, 8.15; N, 1.07. Solution magnetic moment (C_6D_6): 6.00 μ_B. IR (KBr, cm^{-1}): 2960 (s, C–H), 2927 (s, C–H), 2868 (s, C–H), 1585 (s), 1503 (m), 1428 (m), 1276 (m), 1070(m), 940 (s), 853 (m), 750 (s).

Result and Discussions



Scheme 2. Synthesis of a highly sterically demanding amino triphenolate ligand (**6**).

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Synthesis of triisopropylphenyl amino triphenolate (TRIP-ATP). The bulky amino triphenolate ligand was synthesized in six steps from 1-bromo-2,4,6-triisopropylbenzene, with an overall yield of 38% (Scheme 2). From a practical point of view, it is quite efficient that the six-step synthesis of the pure complex ligand was achieved without requiring column chromatography. The simple washing, recrystallization, and sublimation of the as-synthesized products provided analytically pure compounds. The facile purification process enables multi-gram scale synthesis of the ligand **6**. The synthesis involved the palladium-catalyzed Kumada coupling reaction of the Grignard reagent (**1**)[12] and 2-bromophenol,[13] followed by *ortho* formylation of the phenol.[14] Protection of phenol by allyl group and amination were proceeded to afford **5**,[15] of which was further deprotected to obtain the final amino triphenol ligand **6**.[16] The successful preparation of other bulky amino triphenol via allyl protection was also patented by Kazuki *et al*.[15] However, other phenol protecting groups such as benzyl[16] and silyl groups that used for the synthesis of other amino triphenolates were not successful because the deprotection of benzyl group and the clean silyl protection were not successful in the ligand system. Therefore, allyl protection seems to be useful for the preparation of amino triphenolates with highly bulky *ortho* substituents on phenols. All new compounds were fully characterized.

Synthesis of transition metal complexes

Most early transition metal complexes (**6-V**, **6-Cr**, and **6-Mn**) of TRIP-ATP were synthesized by phenol deprotonation in the presence of metal salts, except a titanium complex **6-Ti** (Scheme 3). That complex was directly synthesized by transalkoxylation of the ligand **6** with $Ti(O^{i}Pr)_4$ in benzene solution at room temperature. The analytically pure colorless complex (**6-Ti**) was characterized by ^1H and ^{13}C nuclear magnetic resonance (^1H and ^{13}C NMR) spectroscopy. The *Iso*-propoxide and methylene protons of the complex were successfully assigned using ^1H NMR spectroscopy and ^1H–^1H correlated spectroscopy (COSY) (see Supplementary Information). In the case of vanadium and chromium complexes, THF was coordinated to each metal ion, as evidenced by X-crystallographic analysis. In the synthesis of a manganese complex with **6**, several manganese salts, such as hydrated $Mn(acac)_3$ (acac = acetylacetonate), MnF_3, and dried $Mn(acac)_3$, were evaluated for complexation under various conditions. However, only dried $Mn(acac)_3$ afforded the desired and analytically pure complex with **6**. MnF_3 did not react with **6**, and hydrated $Mn(acac)_3$ afforded a poorly crystalline material, whose structure was not confirmed by X-ray analysis. Anhydrous $Mn(acac)_3$ afforded **6-Mn**, where the coordinated acac anion interacted with two sodium cations and THF to increase the complexity of the manganese metal environment (Scheme 3). Interestingly, the net oxidation state of Mn was +2, which possibly originates from the disproportionation of manganese(III) complexes, as evidenced by X-ray crystallography and its solution magnetic moment (6.00 μ_B). We believe that the low isolation yield (26%) of **6-Mn** is associated with the complexity of the Mn coordination geometry and the disproportionation of Mn(III) intermediates. Additionally, almost colorless **6-Mn** shows very weak peaks in the visible region based on UV-Vis spectra, which indicates a spin forbidden character of the Mn(II) with a high spin state (see Supplementary Information). When NaH was replaced by Et_3N, complexation of Mn with **6** was not observed.

Table 1. Selected crystal data and refinement details.

	6-Ti	**6-V**	**6-Cr**	**6-Mn**
Empirical formula	$C_{90}H_{112}NO_4Ti$	$C_{70}H_{92}NO_4V$	$C_{72.5}H_{98}CrNO_4$	$C_{75}H_{99.06}MnNNa_2O_6$
Formula weight	1319.70	1062.38	1099.51	1211.52
Temperature/K	100	100	100	100
Crystal system	trigonal	monoclinic	triclinic	orthorhombic
Space group	R-3	C2/c	P-1	Pbca
a/Å	23.4039(2)	37.206(7)	14.1640(11)	18.612(4)
b/Å	23.4039(2)	14.294(3)	14.4132(11)	27.311(6)
c/Å	24.9083(5)	24.650(5)	18.4865(14)	30.616(6)
α/°	90	90	108.161(3)	90
β/°	90	95.33(3)	91.379(3)	90
γ/°	120	90	110.604(3)	90
Volume/Å³	11815.5(3)	13053(5)	3318.4(4)	15562(5)
Z	6	8	2	8
Radiation	MoKα (λ = 0.71073)	synchrotron (λ = 0.70000)	MoKα (λ = 0.71073)	synchrotron (λ = 0.70000)
R1 [I>=2σ (I)]	0.0784	0.0862	0.0499	0.0682
wR2 [I>=2σ (I)]	0.2231	0.2447	0.1315	0.2089

Solid-state structures of 6-Ti, 6-V, 6-Cr, and 6-Mn. X-ray single crystals of each complex were grown in a proper solvent system at –40 °C. The structures of the monomeric units of the complexes **6-Ti**, **6-V**, **6-Cr** and **6-Mn** are shown in Figure 1. As described in the literature,[17] all complexes adopted a trigonal bipyramidal (TBP) geometry having high geometry index ($\tau \geq 0.87$); most of the early transition metal amino triphenolate complexes have the same geometry. It is interesting that even the highly sterically demanding TRIP does not change the preferential geometry of TBP in the early transition metal complexes, while some cases show octahedral geometry at the metal sites. In the **6-Ti** complex, due to the highly symmetric system (trigonal), the *iso*-propoxide molecule was disordered in three positions. The Ti–O(2) and Ti–N(4) bond distances at the axial position are 1.780 and 2.319 Å, respectively. The Ti–O(1) distance in the equatorial position is 1.843 Å (Figure 1). These bond distances are in good agreement with the values of other amino triphenolate titanium complexes that have been reported.[4d,18] Notably, the equatorial Ti–O(1) distance in **6-Ti** is almost the same as the Ti–O bond distance in the other titanium amino triphenolate complexes with the less sterically hindered methyl group.[5o] This indicates that the TRIP substituent is just adequate for the TBP geometry and provides a hydrophobic environment around the titanium center.

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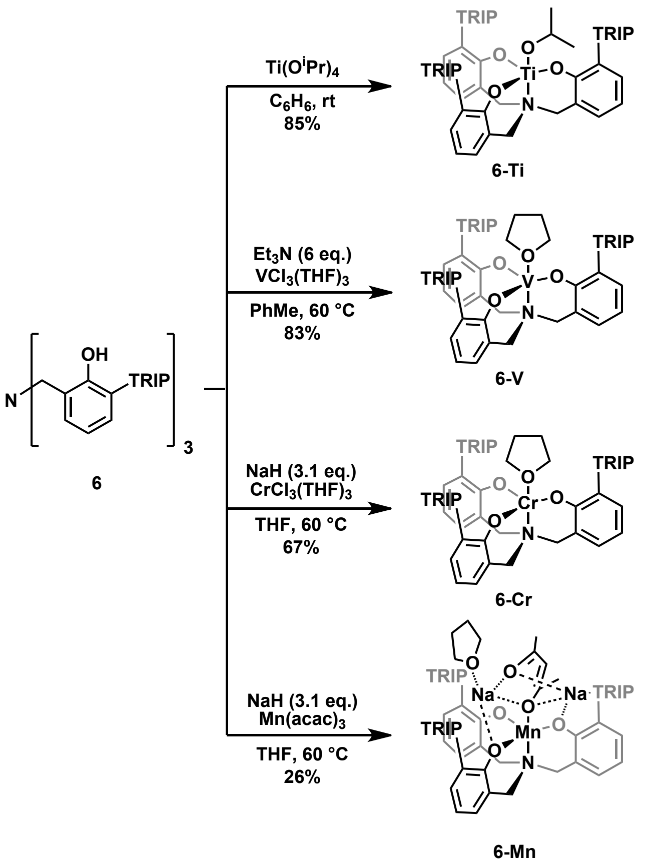

Scheme 3. Synthesis of first-row early transition metal complexes with **6**.

In the vanadium structure (**6-V**), a THF molecule is coordinated in the axial position at a distance of 2.102(2) Å (V–O(4)), while the V–N(6) bond distance is 2.145(3) Å, which is shorter than that of **6-Ti** due to the weaker trans influence of THF. The V–O bond distances in the equatorial position are 1.866(2), 1.874(2) and 1.869(2) Å, affording a typical TBP geometry. These bond distances are in good agreement with the values of the previously reported amino triphenolate vanadium THF complex.[19]

Although numerous amino triphenolate complexes with a variety of transition metal ions have been reported,[7] there have been few structural studies of chromium metal with amino triphenolates. The first X-ray structural study of an amino triphenolate chromium complex was reported in 2018 to the best of our knowledge.[2c] Unlike the published octahedral geometry of the chromium complex supported by amino triphenolate and two 4-dimethylaminopyridine (DMAP) molecules, **6-Cr** shows a TBP geometry, where the ligand and chromium bond distances are similar to those in the **6-V** complex. A THF molecule and nitrogen atom of **6-Cr** are coordinated to Cr(III) in a trans position at distances of 2.041(1) Å (Cr–O(5)) and 2.067(1) Å (Cr–N(1)); these values are slightly shorter than those of **6-V** due to the higher number of bonding orbital electrons of Cr(III) (d^3) than those of V(III) (d^2). The Cr–O bond distances in the equatorial position are 1.856(2), 1.878(2) and 1.890(2) Å.

Both **6-V** and **6-Cr** complexes, which have a high spin state based on measurements of their magnetic moments using the Evans method,[20] were also analyzed by DFT calculations using the Gaussian09 program.[21] Not surprisingly, the bond distances obtained from the optimized structures at the B3PW91 functional with appropriate basis sets (see Supplementary Information) are in good agreement with the experimental values. Molecular orbital (MO) analysis of both complexes (**6-V** and **6-Cr**) shows that the electron densities of the filled frontier orbitals are localized in the metal sites, while those of the lowest empty frontier orbitals are localized in the ligand phenyl rings (Figures S12, S13 and S14).

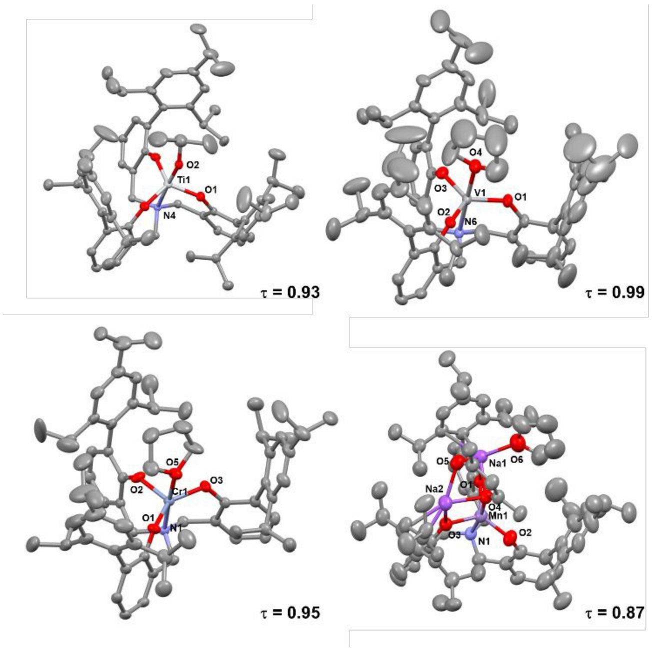

Figure 1. X-ray crystal structures of **6-Ti**, **6-Cr**, **6-V** and **6-Mn** showing thermal ellipsoids at the 50% probability level. Hydrogen atoms were omitted for clarity. Geometry index (τ) values were noted. Selected bond lengths (Å) (computed bond lengths by DFT) and angles (°) for the complexes: **6-Ti**, Ti1–O1 1.843, Ti1–O2 1.780, Ti1–N4 2.319, O1–Ti–O1′ 118.02, N4–Ti–O2 173.8 N4–Ti1–O1 81.85; **6-V**, V1–O1 1.874(2) (1.878), V1–O2 1.866(2) (1.873), V1–O3 1.869(2) (1.872), V1–O4 2.102(2) (2.123), V1–N6 2.145(3) (2.137) O1–V1–O2 120.16(9) N6–N1–O4 179.3(1) N6–V1–O1 90.94(9); **6-Cr**, Cr1–O1 1.878(2) (1.895), Cr1–O2 1.856(2) (1.888), Cr1–O3 1.890(2) (1.897), Cr1–N1 2.067(1) (2.059) N1–Cr1–O5 176.59(7) O1–Cr1–O2 108.43(7) N1–Cr1–O1 91.06(7); **6-Mn**, Mn1–O1 2.093(2), Mn1–O2 2.006(2), Mn1–O3 2.091(2), Mn1–N1 2.238(2) N1–Mn1–O4 172.42(8) O1–Mn1–O2 125.63(8) N1–Mn1–O1 89.88(8).

Structural studies of manganese with an amino triphenolate are also rare, probably due to the synthetic difficulty that we experienced. The first X-ray crystal structure was reported by the Meyer group in 2014.[5d] The group successfully isolated and characterized a manganese amino triphenolate complex with an empty coordinate site at the axial position by X-ray crystallography. The key to the successful isolation was to utilize an adamantly group as a bulky substituent and bis(triphenylphosphine)iminium (PNP) cation. Due to the highly soluble character of **6**, unstable single crystals of **6-Mn** were analyzed using a synchrotron X-ray source. Although the manganese oxidation state of **6-Mn** is somewhat confused due to the different oxidation state of the precursor ($Mn(acac)_3$), the X-ray crystal structure of **6-Mn** clearly indicates that manganese has the +2 oxidation state, evidenced by the sum (-2) of amino triphenolate, one acac, and two sodium cations (Figure 2). In the core structure, two sodium cations interact tightly with the two benzene rings of **6**, acac, and one THF molecule, while Mn adopts a TBP geometry with relatively long equatorial Mn–O distances (2.091(2), 2.006(2), and 2.093(2) Å). The axial distances to Mn are 2.147(2) Å (Mn–O(4)) and 2.238(2) Å (Mn–N(1)).

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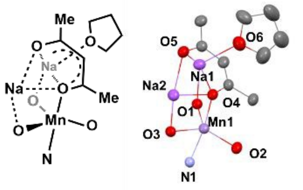
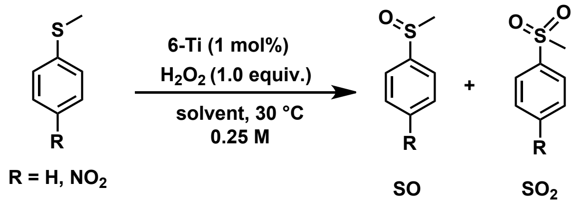


Figure 2. X-ray crystal structures of the **6-Mn** core with thermal ellipsoids at the 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) for **6-Mn**, Mn1–O4 2.147(2), O1-Na1 2.336(2), O3-Na2 2.242(2), O5-Na2 2.369(3), O5-Na1 2.506(2), Na1-O4 2.368(2).

Solution behaviors of 6-Ti, 6-V, 6-Cr, and 6-Mn. Diamagnetic **6-Ti** was analyzed by ^{1}H and ^{13}C NMR spectroscopy in benzene solution. **6-Ti** presented two doublets at 4.16 and 2.66 ppm corresponding to two benzyl protons; such a large difference was already noted by the Brown group.[18] ^{1}H–^{1}H COSY NMR data clearly show the correlation of methine and isopropyl protons of the *iso*-propoxide. Unlike diamagnetic **6-Ti**, magnetic properties of **6-V**, **6-Cr** and **6-Mn** in the solution phase were measured by the Evans method. The solution magnetic moment of **6-V** in C_6D_6 was 2.66 μ_B, which is consistent with an S = 1 complex having the d^2 configuration of V^{3+}. The magnetic moments of **6-Cr** and **6-Mn** were 3.76 μ_B and 6.00 μ_B, respectively, indicating high spin states in both complexes.

Table 2. Sulfoxidation of thioanisoles catalyzed by 6-Ti.



entry	R	solvent	time	conv. (%)	SO:SO$_2$
1	H	CD_3CN	3 h	81	64:36
2	H	MeOD	10 min	97	99:1
3	H	$CDCl_3$	3 h	44	85:15
4	NO_2	C_6D_6	6 h	43	66:34
5	NO_2	CD_3CN	1 h	93	64:36
6	NO_2	MeOD	40 min	99	90:10
7	NO_2	$CDCl_3$	3 h	34	98:2

Conversion and selectivity were measured by ^{1}H NMR spectroscopy using 1,2-dichloroethane as an internal standard. Without **6-Ti**, no conversion was observed for both thioanisoles.

Sulfoxidation catalyzed by 6-Ti. To study the catalytic behaviour of the transition complexes, we first investigated **6-Ti** for the oxidation of thioanisole by aqueous hydrogen peroxide. The Licini group reported the sulfoxidation of thioanisoles catalyzed by a titanium complex supported by simple amino triphenolates.[4a] Inspired by this work, we wanted to evaluate the steric effect of **6-Ti** to assess the selectivity in sulfoxidation of thioanisole and overoxidation to sulfone. The sulfoxidation of thioanisoles was very efficient in methanol, as the reaction rate, conversion, and selectivity of sulfoxidation in methanol were superior to that in other solvents (Table 2). Especially, sulfoxidation of 4-nitrothioanisole, which possesses an electron-withdrawing group, afforded 99% conversion with 9:1 selectivity (entry 6). Compared with the results from the previous report,[4a] the bulky titanium complex **6-Ti** showed better catalytic sulfoxidation regarding faster reaction time, increased conversion rate and selectivity.

Table 3. Ethylene polymerization catalyzed by 6-Cr.[a]

entry	solvent	yield (g)	activity[b]	T_m (°C)[c]	χ (%)[d]	M_w (kg/mol)[e]	PDI [e,f]
1	MeCy[g]	0.183	73.2	134.6	81	152	13.4
2[h]	MeCy[g]	0.006	2.4	-	-	-	-
3	PhMe[g]	0.120	48.0	135.4	51	996	93.2
4[h]	PhMe[g]	0.015	6.0	-	-	-	-

[a] General reaction conditions: 5 μmol **6-Cr**, 250 equivalents DMAO, 50 mL of solvent, 20 bar ethylene pressure, 40 °C, 30 min. [b] In units of [kg of PE·(mol Cr)$^{-1}$·h^{-1}. [c] Determined by differential scanning calorimetry. [d] Crystallinity (%) = ($\Delta H_m/\Delta H_m$*) x 100, where ΔH_m = measured melting enthalpy, ΔH_m* = theoretical value for purely crystalline polyethylene (ca. 293 J/g). [e] Determined by high-temperature gel permeation chromatography. [f] Polydispersity index (PDI) = M_w/M_n. [g] MeCy = methylcyclohexane. PhMe = toluene [h] Control experiment carried out in the absence of **6-Cr**. Not determined (-).

Polymerization of ethylene catalyzed by 6-Cr. Most homogeneous chromium complexes generate a mixture of ethylene oligomers and/or low density polyethylene (PE) with many branches.[22] To date, only a few examples of homogeneous chromium catalysts producing HDPE have been reported.[23] A chromium(III)-based amino triphenolate complex has been investigated for the copolymerization of epoxides and cyclic anhydrides,[2c] but not for ethylene polymerization. We expected that the bulky structure of **6-Cr** would produce a highly linear polyethylene by suppressing chain-walking (re-insertion of β-eliminated olefins).[24] Thus, we carried out ethylene polymerization with **6-Cr** activated by dry methylaluminoxane (DMAO), and the representative results are summarized in Table 3. Notably, activation of **6-Cr**/DMAO in methylcyclohexane as the reaction solvent produced PE of high melting temperatures (134.6 °C) with high crystallinity 81% (entry 1; Figure S3). Also, ^{13}C NMR analysis of this polymer indicated that the PE was highly linear and had almost no branches (Figure S5 (b)). These results suggest that the bulky ligand retards chain walking, resulting in highly linear PE in accordance with our hypothesis.

In addition, we observed that the molecular weight and polydispersity index (PDI) of the resulting PE varied dramatically with the solvent used, whereas the thermal properties of PE were insensitive to the reaction solvent. For example, ethylene polymerization using **6-Cr**/DMAO in methylcyclohexane yielded PE with M_w of 152 kg/mol and PDI of 13.4 (entry 1). In contrast, the same catalytic system using toluene as the solvent produced PE with a high melting temperature of 135.4 °C (Figure S4), but with much broader polydispersity (PDI = 93.2, M_w = 996 kg/mol; entry 3). A nearly unimodal distribution was observed for PE obtained using methylcyclohexane, while the PE produced in toluene displayed a clearly multimodal distribution with a high molecular weight fraction being dominant (Figure S5 (a)). The probable source of the broad multimodal distribution of PE is the formation of different active species after activation by the aluminum cocatalyst. The catalytic performance of **6-Cr** was confirmed by the control experiments carried out in the absence of **6-Cr**, but under otherwise identical conditions (entries 1 vs. 2, entries 3 vs. 4).

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Conclusion

In summary, we successfully demonstrated the synthesis and characterization of the highly sterically demanding amino triphenolate ligand and its early-transition metal complexes. All metal complexes adopted the TBP geometry and the oxygen atom of *iso*-propoxide, THF or acac was bound to the metal in the axial position. However, the manganese complex, which was presumably obtained by disproportionation of manganese(III) complexes, was more complex, with sodium cations that bound to the oxygen atoms of acac and the ligand. The titanium complex was used for sulfoxidation of thioanisoles, which showed high conversion and selectivity. Additionally, the bulkiness of the chromium complex enabled the preparation of a highly linear PE, presumably due to suppression of chain walking. We believe that this new bulky ligand system provides novel reactivity and is a robust catalytic platform for various organic transformations. Applications to additional catalytic reactions and the synthesis of other transition metal complexes are being studied.

Conflicts of interest

There are no conflicts to declare.

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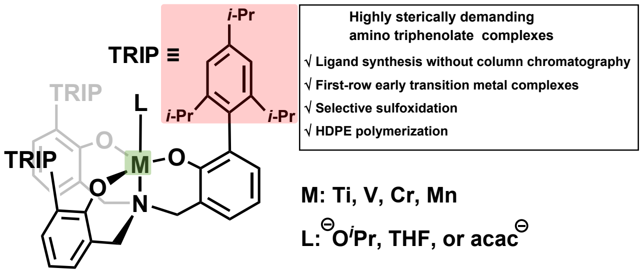

A highly sterically demanding amino triphenolate ligand was successfully synthesized, and early transition metal complexes (Ti, V, Cr, and Mn) supported by the ligand were also obtained and fully characterized.

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