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Synthesis, Characterization, and Norbornene Polymerization Behavior of the Half-Sandwich Complexes [Cp*$_3$M$_3$(μ_3-L)Cl$_3$] and [Cp*M(2-SPyH)Cl$_2$] (M = Ir, M = Rh, [L]$^{3-}$ = 1,3,5-Triazine-2,4,6-trithiolato, 2-SPy = 2-Pyridinethione)

Ying-Feng Han, Yuan-Biao Huang, Yue-Jian Lin, and Guo-Xin Jin*

Shanghai Key Laboratory of Molecular Catalysis and Innovative Material, Department of Chemistry,
Fudan University, Shanghai, 200433, People's Republic of China

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The trinuclear complexes [Cp*$_3$M$_3$(μ_3-L)Cl$_3$] (**3a**, M = Ir; **3b**, M = Rh; [L]$^{3-}$ = 1,3,5-triazine-2,4,6-trithiolato) have been synthesized via the reactions of the bridging oxalato complexes [Cp*$_2$M$_2$(μ-C$_2$O$_4$)Cl$_2$] (**2a**, M = Ir; **2b**, M = Rh) with the trisodium salt of 1,3,5-triazine-2,4,6-trithiol (Na$_3$L), respectively. The reactions of half-sandwich iridium and rhodium complexes [Cp*MCl(μ-Cl)]$_2$ with 2-pyridinethione gave the corresponding mononuclear complexes [Cp*M(2-SPyH)Cl$_2$] (**4a**, M = Ir; **4b**, M = Rh). All complexes have been characterized by elemental analyses and NMR and IR spectroscopy. The molecular structures of **3a**,**b** and **4a**,**b** have been determined by X-ray crystallography. The trinuclear iridium complex **3a** shows catalytic activities for the polymerization of norbornene in the presence of methylaluminoxane (MAO) as cocatalyst.

Introduction

1,3,5-Triazine-2,4,6-trithiol (H$_3$L) (also known as 2,4,6-trimercaptotriazine or trithiocyanuric acid), which exists in either the thiol or thione form, and its trisodium salt (Na$_3$L) are widely applied in industry, analytical chemistry, and biochemistry. They are effective analytical reagents to remove univalent and divalent heavy metals (Hg^{2+}, Ag^{+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Hg^{+}, Tl^{+}) from wastewater.[1] The ligand [L]$^{3-}$ ([L]$^{3-}$ = 1,3,5-triazine-2,4,6-trithiolato), bearing three N,S donor sets, can display a great versatility of coordination, including as a monodentate N or S donor,[2] a bidentate chelating [N,S]$^{-}$ donor,[3] or a bridge between two metal ions through the two bidentate [N,S]$^{-}$ donor sets.[4]

When the trisodium salt of trithiocyanuric acid utilizes its three N,S-bidentate sites, four-membered chelate rings can be formed. To our knowledge, there are only two sets of metal complexes, [{(η^5-CH$_3$C$_5$H$_4$)$_2$Ti$^{\mathrm{III}}$}$_3$(μ_3-L)][5] and [{(L′)$_2$Ru$^{\mathrm{II}}$}$_3$(μ_3-L)]$^{3+}$ (L′ = 2,2-bipyridine, 1,10-phenanthroline, arylazopyridine),[6] where the trinucleating mode of [L]$^{3-}$ using all three available [N,S]$^{-}$ donor sets have been reported.

Meanwhile, tautomeric systems were found to be useful in biological systems: for example, RNA transcription, DNA replication, and control of the behavior of nucleic acids. Of the many tautomeric systems,[7a] the simplest example is pyridine-2-thiolate (2-HSPy) and its analogues, which are capable of bonding to metals as either pyridine-2-thiol or pyridine-2-thione.[7b,e] The ligand may be coordinated as a monodentate group through the sulfur or nitrogen atom, as a bidentate chelating moiety through the sulfur and nitrogen donors, or as a bridging ligand through both donor groups.

However, trinucleating motifs of half-sandwich iridium and rhodium complexes have not been developed up to now. Herein we report the synthesis and characterization of the two trinuclear complexes [Cp*$_3$M$_3$(μ_3-L)Cl$_3$] (**3a**, M = Ir; **3b**, M = Rh; [L]$^{3-}$ = 1,3,5-triazine-2,4,6-trithiolato), where the bridging unit [L]$^{3-}$ functions as a tris-bidentate [N,S]$^{-}$ donor ligand. To our knowledge, these are the first examples of half-sandwich iridium and rhodium complexes of 1,3,5-triazine-2,4,6-trithiol in which [L]$^{3-}$ functions as a symmetrical tris-bidentate bridging ligand. Two mononuclear complexes, [Cp*M(2-SPyH)Cl$_2$] (**4a**, M = Ir; **4b**, M = Rh), were obtained via reacting the half-sandwich iridium and rhodium complexes [Cp*MCl(μ-Cl)]$_2$ with 2-pyridinethione.

Results and Discussion

Synthesis and Characterization. The binuclear complexes [Cp*$_2$M$_2$(μ-C$_2$O$_4$)Cl$_2$] (**2a**, M = Ir; **2b**, M = Rh) can be easily synthesized in high yields from the half-sandwich iridium and rhodium dichloride complexes [Cp*MCl(μ-Cl)]$_2$ (**1a**, M = Ir;

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* To whom correspondence should be addressed. Tel: +86-21-65643776. Fax: + 86-21-65641740. E-mail: gxjin@fudan.edu.cn.

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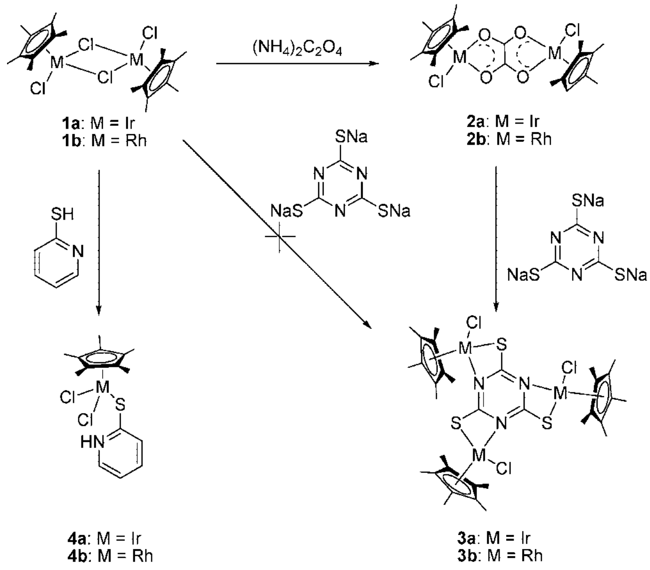
Scheme 1. Syntheses of Complexes 3a,b and 4a,b



1b, M = Rh) with $(NH_4)_2C_2O_4$ in CH_3OH solution, respectively. The IR spectra showed a strong band at about 1620 cm^{-1}, owing to the C=O stretching of the oxalate ligand,[8–11] which is different from the two bands between 1650 and 1750 cm^{-1} observed in most η^2-C_2O_4 complexes.[8,10–13]

When the bridging oxalato complex **2a** was reacted with the trisodium salt of 1,3,5-triazine-2,4,6-trithiol (Na_3L) in the molar ratio 3:2 in CH_2Cl_2, the trinuclear complex $[Cp^*{}_3M_3(\mu_3\text{-L})Cl_3]$ (**3a**, M = Ir, $[L]^{3-}$ = 1,3,5-triazine-2,4,6-trithiolato) was obtained as red prismatic crystals in 89% yield (Scheme 1). In addition, the analogous product $[Cp^*{}_3Rh_3(\mu_3\text{-L})Cl_3]$ (**3b**, $[L]^{3-}$ = 1,3,5-triazine-2,4,6-trithiolato) was also obtained as red prismatic crystals by the same method in 84% yield. However, the direct reaction of the trisodium salt of 1,3,5-triazine-2,4,6-trithiol (Na_3L) with the half-sandwich iridium and rhodium dichloride complexes $[Cp^*MCl(\mu\text{-Cl})]_2$ (**1a**, M = Ir; **1b**, M = Rh) following the same method, does not afford **3a**,**b**.[14]

In the solid-state IR spectra of complexes **3a**,**b** the strong absorption bands at about 1630 cm^{-1} have disappeared, which

Table 1. Selected Bond Distances (Å) and Angles (deg) for 3a,b

	Compound **3a**		
	Bond Distances		
Ir(1)−N(1)	2.115(8)	Ir(1)−Cl(1)	2.386(3)
Ir(1)−S(1)	2.451(3)	Ir(2)−N(2)	2.128(8)
Ir(2)−Cl(2)	2.394(3)	Ir(2)−S(2)	2.430(3)
Ir(3)−N(3)	2.113(7)	Ir(3)−Cl(3)	2.376(3)
Ir(3)−S(3)	2.443(3)	N(1)−C(2)	1.339(13)
N(1)−C(1)	1.374(12)	N(2)−C(3)	1.324(12)
N(2)−C(2)	1.374(12)	N(3)−C(1)	1.336(13)
N(3)−C(3)	1.356(12)	S(1)−C(1)	1.700(11)
S(2)−C(2)	1.690(10)	S(3)−C(3)	1.704(10)
	Bond Angles		
N(1)−Ir(1)−Cl(1)	86.2(2)	N(1)−Ir(1)−S(1)	66.5(2)
Cl(1)−Ir(1)−S(1)	90.44(11)	N(2)−Ir(2)−Cl(2)	80.4(2)
N(2)−Ir(2)−S(2)	66.6(2)	Cl(2)−Ir(2)−S(2)	89.21(12)
N(3)−Ir(3)−Cl(3)	88.3(2)	N(3)−Ir(3)−S(3)	66.7(2)
Cl(3)−Ir(3)−S(3)	90.69(11)	C(2)−N(1)−Ir(1)	139.2(7)
C(1)−N(1)−Ir(1)	102.6(6)	C(3)−N(2)−Ir(2)	136.8(7)
C(2)−N(2)−Ir(2)	100.8(6)	C(1)−N(3)−Ir(3)	139.8(7)
C(3)−N(3)−Ir(3)	102.1(6)	C(1)−S(1)−Ir(1)	81.3(4)
C(2)−S(2)−Ir(2)	81.2(4)	C(3)−S(3)−Ir(3)	80.5(4)
N(3)−C(1)−S(1)	128.8(8)	N(1)−C(1)−S(1)	109.5(7)
N(1)−C(2)−S(2)	128.5(8)	N(2)−C(2)−S(2)	109.9(7)
N(2)−C(3)−S(3)	126.5(8)	N(3)−C(3)−S(3)	110.3(7)
	Compound **3b**		
	Bond Distances		
Rh(1)−N(1)	2.123(4)	Rh(1)−Cl(1)	2.4011(16)
Rh(1)−S(1)	2.4320(15)	Rh(2)−N(2)	2.125(4)
Rh(2)−Cl(2)	2.3842(17)	Rh(2)−S(2)	2.4371(14)
Rh(3)−N(3)	2.125(4)	Rh(3)−Cl(3)	2.3941(16)
Rh(3)−S(3)	2.4549(15)	S(1)−C(1)	1.695(5)
S(2)−C(2)	1.696(5)	S(3)−C(3)	1.701(5)
N(1)−C(2)	1.341(6)	N(1)−C(1)	1.360(6)
N(2)−C(3)	1.340(6)	N(2)−C(2)	1.350(6)
N(3)−C(1)	1.340(6)	N(3)−C(3)	1.364(6)
	Bond Angles		
N(1)−Rh(1)−Cl(1)	82.06(11)	N(1)−Rh(1)−S(1)	66.85(11)
Cl(1)−Rh(1)−S(1)	91.40(6)	N(2)−Rh(2)−Cl(2)	89.73(12)
N(2)−Rh(2)−S(2)	67.04(11)	Cl(2)−Rh(2)−S(2)	92.28(6)
N(3)−Rh(3)−Cl(3)	87.93(12)	N(3)−Rh(3)−S(3)	66.83(11)
Cl(3)−Rh(3)−S(3)	92.00(6)	C(1)−S(1)−Rh(1)	80.01(17)
C(2)−S(2)−Rh(2)	80.00(16)	C(3)−S(3)−Rh(3)	80.36(17)
C(2)−N(1)−Rh(1)	136.4(3)	C(1)−N(1)−Rh(1)	100.0(3)
C(3)−N(2)−Rh(2)	140.8(3)	C(2)−N(2)−Rh(2)	100.4(3)
C(1)−N(3)−Rh(3)	140.6(3)	C(3)−N(3)−Rh(3)	101.4(3)
N(3)−C(1)−S(1)	127.0(4)	N(1)−C(1)−S(1)	110.9(3)
N(1)−C(2)−S(2)	125.4(4)	N(2)−C(2)−S(2)	112.0(3)
N(2)−C(3)−S(3)	126.8(4)	N(3)−C(3)−S(3)	111.2(3)

indicated the absence of the coordinated oxalate ligands. The ^1H NMR spectra showed a singlet at δ 1.83 ppm for **3a**,**b** due to Cp* protons. Detailed structures of complexes **3a**,**b** were confirmed by X-ray analyses.

Crystals of **3a**,**b** suitable for X-ray diffraction study were obtained by slow diffusion of ether into a concentrated solution of the complexes in CH_2Cl_2. Selected bond lengths and angles of **3a**,**b** are given in Table 1.

The crystal structures of the representative trinuclear complexes **3a**,**b** with the atom-numbering scheme are depicted in Figures 1 and 2. The molecular structures indicate that the bridging ligand $[L]^{3-}$ is bonded to the three metal centers using all three available $[N,S]^-$ donor sets in **3a**,**b**, which give three four-membered chelate rings, respectively. The coordination sphere of the metal can be described as a distorted octahedron, if the coordination number of the Cp* ligand is taken to be 3. The Ir−S distances (2.430(3), 2.443(3), 2.451(3) Å) in **3a** and the Rh−S distances (2.4320(15), 2.4371(14), 2.4549(15) Å) in **3b** are similar to the Ru−S distances (2.430(3), 2.437(3), 2.434(3) Å) in $[\{(NpC_5H_4{-}N{=}N{-}C_6H_5)_2Ru\}_3(\mu_3\text{-L})](ClO_4)_3$.[6b]

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(14) A complex mixture of unidentified materials was obtained when the half-sandwich iridium or rhodium dichloride complexes $[Cp^*MCl_2]_2$ (**1a**, M = Ir; **1b**, M = Rh) and the trisodium salt of 1,3,5-triazine-2,4,6-trithiol (Na_3L) were mixed in CH_2Cl_2.

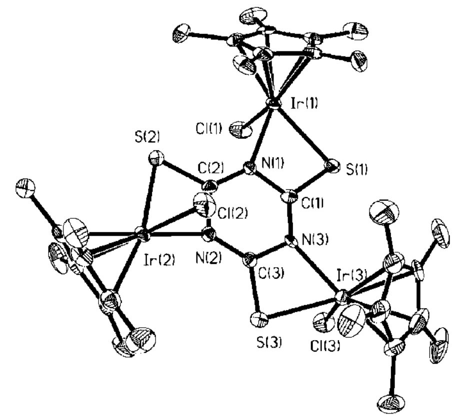

Figure 1. Molecular structure of the trinuclear complex **3a** with thermal ellipsoids drawn at the 30% level. All hydrogen atoms are omitted for clarity.

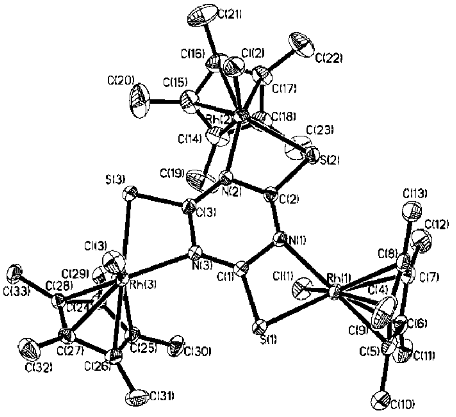

Figure 2. Molecular structure of the trinuclear complex **3b** with thermal ellipsoids drawn at the 30% level. All hydrogen atoms are omitted for clarity.

The Ir−N bond lengths, which range from 2.113(7) to 2.128(8) Å in **3a**, and the Rh−N bond lengths, which range from 2.123(4) to 2.125(4) Å in **3b**, are slightly longer than the Ru−N distances (2.105(7) Å (average)) in $[\{(NpC_5H_4{-}N{=}N{-}C_6H_5)_2Ru\}_3(\mu_3\text{-}L)](ClO_4)_3$.[6b]

The Ir−Cl bond lengths are in the range 2.376(3)–2.394(3) Å for **3a**, and the Rh−Cl bond lengths are in the range 2.3842(17)–2.4011(16) Å for **3b**. The Ir−S−C bond angles are 80.5(4), 81.3(4), and 81.2(4)° in **3a**, and the Rh−S−C bond angles are 80.00(16), 80.01(17), and 80.36(17)° in **3b**.

When the half-sandwich iridium and rhodium complexes $[Cp^*IrCl(\mu Cl)]_2$ (**1a**) and $[Cp^*RhCl(\mu\text{-}Cl)]_2$ (**1b**) were reacted with 2-pyridinethione in a 1:2 molar ratio at room temperature, mononuclear complexes with the ligand coordinated as a monodentate group through a sulfur atom, formulated as $[Cp^*M(2\text{-}SPyH)Cl_2]$ (**4a**, M = Ir, **4b**, M = Rh), were formed in high yields. On the other hand, the reaction of the half-sandwich iridium complex $[Cp^*IrCl(\mu\text{-}Cl)]_2$ (**1a**) with 2-pyridinethione and CH_3ONa in a 1:2:2 molar ratio gave a complex formulated as $[Cp^*Ir(2\text{-}SPy)Cl]$, as reported by Suzuki et al.[15a] In addition, the organometallic mercaptopyridine complex $Cp^*Rh^{III}(PyS)_2$, with metal-mediated tautomerism via the reaction of $[Cp^*RhCl(\mu\text{-}Cl)]_2$ (**1b**) with K[PyS] in a 1:4 molar ratio in CH_3OH, has been reported by Jung et al.[15b] In this complex, one PyS ligand bonds to the rhodium ion as a monodentate S donor, while the other ligand chelates to the metal as a bidentate $[N,S]^-$ donor.

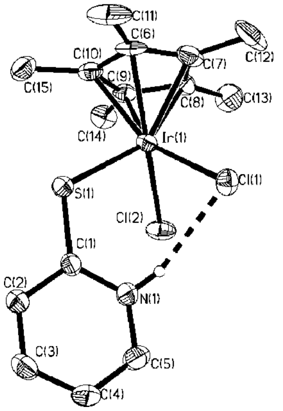

Figure 3. Molecular structure of complex **4a** with thermal ellipsoids drawn at the 30% level.

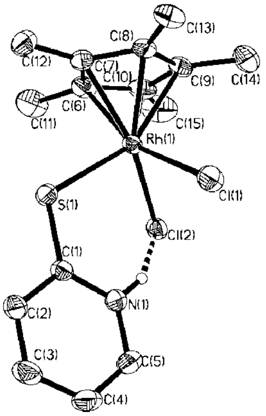

Figure 4. Molecular structure of complex **4b** with thermal ellipsoids drawn at the 30% level.

The ^1H NMR spectraum for **4a** showed two sharp singlets at δ 1.67 and 14.74 ppm due to Cp* protons and N−H and four resonances at δ 6.95, 7.53, 7.76, and 8.08 ppm for 2-pyridinethione protons; that for **4b** also showed two singlets at δ 1.70 and 13.40 ppm due to Cp* protons and N−H and four resonances at δ 6.85, 7.42, 7.61, and 7.68 ppm for 2-pyridinethione protons.

Perspective drawings of **4a**,**b** with the atomic numbering schemes are given in Figures 3 and 4, respectively, and selected bond lengths and angles are given in Table 2. The crystal units of **4a**,**b** consist of the molecule with a $Cp^*{-}M^{III}$ half-sandwich tripod structure, in which one of the "legs" is the S atom from the pyridine-2-thiolato ligand and the other two "legs" are Cl atoms. The Ir−S distance (2.357(9) Å) is much shorter than those found in **3a** (2.430(3), 2.443(3), 2.451(3) Å), but the Ir−S distance is significantly longer than those in the "pseudo-aromatic" iridadithiolene ring in $Cp^*Ir[S_2C_2(B_{10}H_{10})]$ (2.252(5) and 2.251(6) Å).[16]

The Rh−S distance (2.3776(8) Å) is also much shorter than those found in **3b** (2.4320(15), 2.4371(14), 2.4549(15) Å), but the distance is in the normal range of Rh−S single bonds and is similar to that observed in $Cp^*Rh(\eta^2\text{-}2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)(\eta^1\text{-}$

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Table 2. Selected Bond Distances (Å) and Angles (deg) for 4a,b

Compound **4a**			
Bond Distances			
Ir(1)−S(1)	2.357(9)	Ir(1)−Cl(2)	2.425(10)
Ir(1)−Cl(1)	2.438(10)	S(1)−C(1)	1.709(7)
N(1)−C(1)	1.335(7)	N(1)−C(5)	1.361(8)
Bond Angles			
S(1)−Ir(1)−Cl(1)	92.66(10)	C(1)−S(1)−Ir(1)	116.04(18)
C(1)−N(1)−C(5)	123.9(5)	N(1)−C(1)−C(2)	116.3(5)
N(1)−C(1)−S(1)	122.8(4)	C(2)−C(1)−S(1)	120.8(4)
Compound **4b**			
Bond Distances			
Rh(1)−S(1)	2.3776(8)	Rh(1)−Cl(1)	2.4330(8)
Rh(1)−Cl(2)	2.4349(9)	S(1)−C(1)	1.713(3)
N(1)−C(1)	1.342(3)	N(1)−C(5)	1.351(4)
Bond Angles			
S(1)−Rh(1)−Cl(1)	93.32(3)	S(1)−Rh(1)−Cl(2)	93.71(3)
Cl(1)−Rh(1)−Cl(2)	89.22(3)	C(1)−S(1)−Rh(1)	114.98(9)
N(1)−C(1)−C(2)	116.4(2)	N(1)−C(1)−S(1)	122.2(2)
C(2)−C(1)−S(1)	121.3(2)	C(1)−N(1)−C(5)	123.9(3)

$2\text{-SC}_5\text{H}_3\text{N-3-SiMe}_3$) (2.374 (7) Å)[17] and is also similar to the Rh−S distance (2.3799(9) Å) in $\text{Cp*Rh}^{\text{III}}(\text{PyS})_2$, in which the PyS ligand bonds to the rhodium ion as a monodentate S donor.[15b]

The C−S distances 1.709(7) Å in **4a** and 1.713(3) Å in **4b** are longer than the corresponding bonds in **3a** (1.700(11), 1.690(10), 1.704(10) Å) and **3b** (1.695(5), 1.696(5), 1.701(5) Å). In addition, the C−S distances are also longer than those found in the free PySH ligand (1.692(2) Å);[18] the C(1)−S(1)−Ir(1) angle (116.04(18)°) in **4a** is greater than the analogous C(1)−S(1)−Rh(1) angle (114.98(9)°) in **4b**.

An obvious hydrogen bond in **4a** is present with a N−H···Cl(1) distance of 2.375 Å. The N−H···Cl(1) angle is 154.38°. The N−H···Cl(2) distance in **4b** of 2.406 Å also displays the existence of a hydrogen bond, and the N−H···Cl(2) angle is 146.80°.[19]

Norbornene Polymerization. In our previous report,[20] the C,N-chelated metal complex [Ir(Cp*)Cl(Cab$^{\text{N}}$)] is the precursor for a catalyst moderately active in ethylene polymerization. A trinuclear iridium complex has never been used in norbornene (NB) polymerization before.

Preliminary experiments have indicated that the trinuclear iridium complex is not able to catalyze norbornene polymerization without cocatalysts. As we all know, MAO alone is also inactive for norbornene polymerization. Interestingly, in combination with MAO, the trinuclear iridium complex exhibits moderate catalytic activity for norbornene polymerization under moderate conditions. The norbornene polymerization results are summarized in Table 3. However, the analogous trinuclear rhodium showed low activity under the same conditions. The MAO/**3a** ratios also affect the activity and molecular weights. When MAO/**3a** = 5000, the activity of the **3a** reached the maximum value (5.57 × 10^4 g of PNB (mol of Ir)$^{-1}$ h^{-1}). With the MAO/**3a** ratios still rising, the activity of **3a** decreased slightly, while the M_v value of the polymer decreased sharply from 8.82 × 10^5 to 3.98 × 10^5 g mol^{-1}. The activated complex becomes more unstable at higher temperature, so that the highest activity found at 25 °C is the result of a compromise between these two factors. In comparison to the highly active nickel complexes (10^6−10^8 g of PNB (mol of Ni)$^{-1}$ h^{-1})[21] and palladium complexes (10^7g of PNB (mol of Pd)$^{-1}$ h^{-1}),[21c,22] the trinuclear iridium complex showed moderate activity, which is similar to the case for the early transition metals,[23] (pyridyl bis-imine)iron(II) and -cobalt(II) complexes,[24] and copper[21f,25] complexes for norbornene addition polymerization.

Table 3. Norbornene Polymerization for the 3a/MAO Catalytic System[a]

entry	[Ir] (μmol)	MAO/[Ir]	*t* (°C)	yield/g	conversn (%)	activity[b]	M_v[c]
1	3.0	500	25	0.068	2.4	2.27	8.34
2	3.0	1000	25	0.099	3.5	3.30	5.76
3	3.0	2000	25	0.062	2.2	3.10	7.89
4	3.0	4000	25	0.074	2.6	2.47	8.82
5	3.0	5000	25	0.167	5.9	5.57	3.98
6	3.0	5000	50	0.028	1.0	0.9	
7	3.0	5000	70	0.017	0.6	0.6	

[a] Polymerization conditions: [NB]/[**3a**] = 1 × 10^4; time 1 h; V_{total} = 15 mL; solvent chlorobenzene. [b] In units of 10^4 g of PNB (mol of Ir)$^{-1}$ h^{-1}. [c] In units of 10^5 g mol^{-1}, measured in chlorobenzene at 25 °C using the Mark–Houwink coefficients:[23] α = 0.56, K = 5.97 × 10^{-4} dL/g.

All the PNB species obtained by complex **3a** activated with MAO were characterized by IR and ^{1}H NMR analyses (see the Experimental Section and the Supporting Information). All IR spectra and ^{1}H NMR spectra were similar and characteristic for the addition-type PNB[21–25] and revealed no traces of double bonds which are typical for ROMP (ring-opening metathesis polymerization) PNB.

Conclusion

In this work, the two new half-sandwich *tri*nuclear complexes **3a**,**b**, in which the bridging unit [L]$^{3-}$ functions as a tris-bidentate [N,S]$^-$ donor ligand, have been synthesized via the reactions of the bridging oxalato complexes with the trisodium salt of 1,3,5-triazine-2,4,6-trithiol. The reactions of half-sandwich iridium and rhodium complexes with 2-pyridinethione

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Table 4. Crystallographic Data for Compounds 3a,b and 4a,b

	3a	**3b**	**4a**	**4b**
empirical formula	$C_{33}H_{45}Cl_3Ir_3N_3S_3$ CH_2Cl_2	$C_{33}H_{45}Cl_3N_3Rh_3S_3\cdot CHCl_3$	$C_{15}H_{20}Cl_2IrNS$	$C_{15}H_{20}Cl_2RhNS$
fw	1347.78	1114.35	509.48	420.19
cryst syst	monoclinic	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/c$	$P2_1/c$	*Pbca*	*Pbca*
a (Å)	13.265(5)	13.240(5)	9.11(4)	9.0377(16)
b (Å)	24.412(10)	24.318(6)	16.00(7)	16.064(3)
c (Å)	13.705(6)	13.666(3)	23.70(10)	23.757(5)
β(deg)	106.586(6)	106.61(2)	90	90
V (Å^3)	4253(3)	4216(2)	3454(25)	3449.0(11)
Z	4	4	8	8
ρ_{calcd} (g/cm^3)	2.105	1.755	1.960	1.618
μ(Mo Kα) (mm^{-1})	9.853	1.718	8.151	1.411
no. of obsd data	17 560	23 390	15 911	18 632
no. of data/restraints/params	7470/0/457	9142/0/457	3834/1/190	3790/0/190
goodness of fit	1.017	1.042	0.910	1.175
R indices ($I > 2\sigma(I)$)[a]	R1 = 0.0503, wR2 = 0.1190	R1 = 0.0440, wR2 = 0.1205	R1 = 0.0305, wR2 = 0.0651	R1 = 0.0310, wR2 = 0.0763
R indices (all data)	R1 = 0.0656, wR2 = 0.1273	R1 = 0.0602, wR2 = 0.1319	R1 = 0.0461, wR2 = 0.0682	R1 = 0.0370, wR2 = 0.0801
largest peak, hole (e Å^{-3})	2.387, −2.598	1.421, −1.514	1.573, −1.063	0.432, −0.654

[a] $R1 = \sum||F_o| - |F_c||$ (based on reflections with $F_o^2 > 2\sigma F^2$). $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.095P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$ (also with $F_o^2 > 2\sigma F^2$).

gave the corresponding mononuclear complexes **4a**,**b**. A preliminary study showed that the new half-sandwich iridium complex **3a** is the precursor for a catalyst moderately active in norbornene polymerization. To the best of our knowledge, this is the first report on a half-sandwich trinuclear iridium complex in which the bridging unit $[L]^{3-}$ functions as a tris-bidentate $[N,S]^-$ donor ligand exhibiting activity toward polymerization of norbornene.

Experimental Section

General Comments. All manipulations were performed under an atmosphere of nitrogen using standard Schlenk techniques. Dichloromethane and 1,2-dichloroethane were distilled over CaH_2, and hexane was distilled over sodium/benzophenone ketyl just before use. $[Cp^*IrCl_2]_2$ (**1a**)[26] and $[Cp^*RhCl_2]_2$ (**1b**)[26] were prepared according to the reported procedures; 2-pyridinethione was obtained commercially and used without further purification. Methylaluminoxane (MAO) was purchased from Aldrich as a 10 wt % toluene solution and used without further purification. IR spectra were recorded on a Nicolet AVATAR-360 IR spectrometer. Elemental analyses were carried out with a Elementar III Vario EI analyzer. ^1H NMR (500 MHz) spectra were obtained on a Bruker DMX-500 spectrometer in $[D_6]$DMSO or $CDCl_3$ solution.

Synthesis of $[Cp^*_2Ir_2(\mu\text{-}C_2O_4)Cl_2]$ (2a). $(NH_4)_2C_2O_4\cdot H_2O$ (140 mg, 1 mmol) was added to a suspension of $[Cp^*IrCl_2]_2$ (800 mg, 1 mmol) in CH_3OH (20 mL), and the suspension was stirred at 55 °C for 5 h. The solvent was then evaporated to dryness under vacuum; the residue was extracted with CH_2Cl_2 to give red crystals of **2a** (740 mg, 91%). Anal. Calcd for $C_{22}H_{30}Cl_2O_4Ir_2$: C, 32.47; H, 3.72. Found: C, 32.30; H, 3.65. ^1H NMR (500 MHz, $[D_6]$DMSO): δ 1.62 (s, 30H; Cp*) ppm. IR (KBr disk): ν 1620 (s) cm^{-1}.

Synthesis of $[Cp^*_2Rh_2(\mu\text{-}C_2O_4)Cl_2]$ (2b). $(NH_4)_2C_2O_4\cdot H_2O$ (140 mg, 1 mmol) was added to a suspension of $[Cp^*RhCl_2]_2$ (618 mg, 1 mmol) in CH_3OH (20 mL), and the suspension was stirred at 55 °C for 5 h. The solvent was then evaporated to dryness under vacuum; the residue was extracted with CH_2Cl_2 to give red crystals of **2b** (621 mg, 86%). Anal. Calcd for $C_{22}H_{30}Cl_2O_4Rh_2$: C, 41.60; H, 4.76. Found: C, 41.92; H, 4.84. ^1H NMR (500 MHz, $[D_6]$DMSO): δ 1.64 (s, 30H; Cp*) ppm. IR (KBr disk): ν 1612 (s) cm^{-1}.

Synthesis of $[Cp^*_3Ir_3C_3N_3S_3Cl_3]$ (3a). $Na_3C_3N_3S_3$ (24 mg, 0.1 mmol) was added to a solution of **2a** (122 mg, 0.15 mmol) in CH_2Cl_2 (20 mL) at room temperature, and the mixture was stirred for 18 h, followed by filtration to remove insoluble compounds; the filtrate was concentrated to about 3 mL, and diethyl ether was added, giving **3a** as red solids (112 mg, 89%). Anal. Calcd for $C_{33}H_{45}Cl_3Ir_3N_3S_3$: C, 31.38; H, 3.59; N, 3.33. Found: C, 31.53; H, 3.34; N, 3.28. ^1H NMR (500 MHz, $CDCl_3$): δ 1.83 (s, 45H; Cp*) ppm. IR (KBr disk): ν 2964 (w), 2912 (w), 1454 (s), 1381 (w), 1255 (m), 1090 (w), 1029 (w), 896 (w), 803 (w) cm^{-1}.

Synthesis of $[Cp^*_3Rh_3C_3N_3S_3Cl_3]$ (3b). $Na_3C_3N_3S_3$ (24 mg, 0.1 mmol) was added to a solution of **2b** (96 mg, 0.15 mmol) in CH_2Cl_2 (20 mL) at room temperature, and the mixture was stirred for 18 h, followed by filtration to remove insoluble compounds; the filtrate was concentrated to about 3 mL, and diethyl ether was added, giving **3b** as red solids (83 mg, 84%). Anal. Calcd for $C_{33}H_{45}Cl_3Rh_3N_3S_3$: C, 39.83; H, 4.56; N, 4.22. Found: C, 39.59; H, 4.52; N, 4.28. ^1H NMR (500 MHz, $CDCl_3$): δ 1.83 (s, 45H; Cp*) ppm. IR (KBr disk): ν 2963 (w), 2915 (w), 1443 (s), 1381 (w), 1261 (m), 1096 (w), 1023 (w), 887 (w), 799 (w) cm^{-1}.

Synthesis of $[Cp^*Ir(SPy)Cl_2]$ (4a). HSPy (22 mg, 0.2 mmol) was added to a solution of **1a** (80 mg, 0.10 mmol) in CH_2Cl_2 (20 mL) at room temperature, and the mixture was stirred for 18 h. The solution was concentrated to about 3 mL, and diethyl ether was added, giving **4a** as red solids (92 mg, 92%). Anal. Calcd for $C_{15}H_{20}Cl_2IrNS$: C, 35.36; H, 3.96; N, 2.75. Found: C, 35.29; H, 3.75; N, 2.68. ^1H NMR (500 MHz, $CDCl_3$): δ 14.74 (br, 1H; N−H), 8.08 (dd, 1H; J = 6.4, 5.9 Hz, Py-H), 7.76 (d, 1H; J = 8.3 Hz, Py-H), 7.53 (dd, 1H; J = 8.3, 6.4 Hz, Py-H), 6.95 (dd, 1H; J = 6.4, 6.3 Hz, Py-H), 1.67 (s, 15H; Cp*) ppm. IR (KBr disk): ν 3420 (s), 3071 (w), 3017 (w), 2977 (w), 2907 (w), 1579 (s), 1500 (w), 1444 (w), 1378 (w), 1261 (w), 1129 (m), 1082 (w), 1027 (w), 766 (w) cm^{-1}.

Synthesis of $[Cp^*Rh(SPy)Cl_2]$ (4b). HSPy (22 mg, 0.2 mmol) was added to a solution of **1b** (64 mg, 0.10 mmol) in CH_2Cl_2 (20 mL) at room temperature, and the mixture was stirred for 18 h. The solution was concentrated to about 3 mL, and diethyl ether was added, giving **4b** as red solids (78 mg, 91%). Anal. Calcd for $C_{15}H_{20}Cl_2RhNS$: C, 42.87; H, 4.80; N, 3.33. Found: C, 42.17; H, 4.82; N, 3.25. ^1H NMR (500 MHz, $CDCl_3$): δ 13.40 (br, 1H; N−H), 7.68 (dd, 1H; J = 6.4, 5.5 Hz, Py-H), 7.61 (d, 1H; J = 8.7 Hz, Py-H), 7.42 (dd, 1H; J = 8.7, 6.0 Hz, Py-H), 6.85 (dd, 1H; J = 6.4, 6.0 Hz, Py-H), 1.70 (s, 15H; Cp*) ppm. IR (KBr disk): ν 3436 (s), 3190 (w), 3068 (w), 3012 (w), 2962 (w), 2920 (w), 1585 (s), 1484 (w), 1447 (w), 1370 (w), 1261 (w), 1132 (m), 1098 (w), 1025 (w), 804 (w) cm^{-1}.

Catalytic Norbornene Polymerization. In a typical procedure for the norbornene polymerization, the precatalyst, which is the iridium complex in chlorobenzene, was added into a special polymerization bottle (50 mL) with a strong stirrer under a nitrogen

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atmosphere. Then MAO was charged into the polymerization system via syringe. Finally the norbornene, diluted in chlorobenzene, was added to the polymerization system, which started the reaction. After a designated time acidic ethanol (V_{ethanol}:$V_{\mathrm{concd\ HCl}} = 10$:1) was added to terminate the reaction. The PNB was isolated by filtration, washed with ethanol, and dried at 80 °C for 48 h under vacuum. For all polymerization procedures, the total reaction volume was 15 mL, which can be achieved by varying the amount of chlorobenzene when necessary. The viscosity-average molar masses (M_v) of the PNB were obtained in chlorobenzene at 25 °C using the Mark–Houwink coefficients:[23] $\alpha = 0.56$, $K = 5.97 \times 10^{-4}$ dL/g. IR (KBr): 2945 (s), 2869 (s), 1452 (m), 1373 (w), 1296 (w), 1223 (w), 1148 (w), 1109 (w), 1041 (w), 943 (w), 893 (w) cm^{-1}. ^{1}H NMR: δ 0.7–3.0 (m, maxima at 0.91, 1.28, 1.93 ppm).

X-ray Structure Determination. All single crystals were measured on a CCD-Bruker SMART APEX system. All the determinations of unit cell and intersity data were performed with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). All the data were collected at room temperature, and the structures were solved by direct methods and subsequently refined on F^2 by using full-matrix least-squares techniques (SHELXL).[27] SADABS[28] absorption corrections were applied to the data, all non-hydrogen atoms, including solvent molecules in **3a**,**b**, were refined anisotropically, and hydrogen atoms were located at calculated positions. A summary of the crystallographic data and selected experimental details are given in Table 4.

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Supporting Information Available: Figures giving IR and NMR spectra for **3a** and CIF files giving crystallographic data for **3a**,**b** and **4a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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