

Synthesis and characterization of scandium complexes with reduced ligands: Crystal structures of Cp^*ScI_2 , $[\text{Cp}^*\text{ScI}(\text{bpy})]_2$, and $[\text{Cp}^*\text{ScCl}(\text{bpy})]_2$

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Abstract

The synthesis and characterization of complexes containing a $\text{Cp}^*\text{Sc}(\text{R}_2\text{bpy})$ (Cp^* = pentamethylcyclopentadienyl, bpy = 4,4'- $\text{R},\text{R}-2,2'$ -bipyridine, $\text{R} = \text{H}, \text{Me}$) motif are described. Cp^*ScI_2 (**1**) was prepared from $\text{Cp}^*\text{Sc}(\text{acac})_2$ (acac = acetylacetonate) and AlI_3 (2 equiv) in pentane. Compound **1** reacted with bipyridine and 4,4'-dimethyl-2,2'-bipyridine (dmb) in benzene to yield $\text{Cp}^*\text{ScI}_2(\text{bpy})$ (**3**) and $\text{Cp}^*\text{ScI}_2(\text{dmb})$ (**4**), respectively. Compound **3** was reduced by alkali metal reductants such as Na/Hg , NaK_2 , and K in aromatic solvents to yield $[\text{Cp}^*\text{ScI}(\text{bpy})]_2$ (**5**). The chloride analog of **5**, $[\text{Cp}^*\text{ScCl}(\text{bpy})]_2$ (**7**), was prepared from Cp^*ScCl_2 by salt metathesis with $\text{Li}_2(\text{dme})_2\text{bpy}$ (**6**) (dme = dimethoxyethane) in toluene. Compounds **1**, **5**, and **7** have been structurally characterized. Analysis of the bond distances of the bipyridine ligands in **5** and **7**, together with infrared and UV/vis spectroscopic data, suggest that the bipyridine ligands in these molecules exist as radical anions. The bipyridine ligands in **5** and **7** are arranged co-facially and are in close proximity ($\leq 3.30 \text{ \AA}$), suggesting the presence of a π - π interaction.

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1. Introduction

The chemistry of scandium is dominated by the +3 oxidation state, and until the early nineties no molecular scandium compounds in other oxidation states had been reported. In 1991, Cloke and coworkers reported the synthesis of zero- and mono-valent scandium complexes by metal vapor synthetic techniques [1]. Since that report, only a few other low valent scandium complexes

have appeared in the literature [2–6]. Most recently, Hessen and coworkers reported the synthesis of a 1,3-diene complex of scandium that displayed reactivity similar to that of other low valent early transition metal complexes, and unlike that expected for a d^0 metal center [7].

In this contribution, we report attempts to synthesize low valent scandium complexes by reduction of scandium(III) precursors with alkali metal derivatives. By this route, we have been able to obtain and characterize $[\text{Cp}^*\text{ScI}(\text{bpy})]_2$ (Cp^* = pentamethylcyclopentadienyl, bpy = 2,2'-bipyridine) and $[\text{Cp}^*\text{ScCl}(\text{bpy})]_2$. Analytical data suggests that these compounds are best described as containing scandium(III) centers complexed by bipyridine radical anions.

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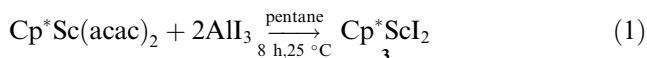
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2. Results and discussion

2.1. Synthesis of scandium(III) precursors

Metal iodides are often employed as precursors to low valent group 4 [8–10] and group 13 [11–13] complexes since reductions of metal iodides often produce higher product yields than reductions of analogous bromides and chlorides. For example, Roesky and coworkers found that reduction of $[\text{Cp}^*\text{AlX}_2]_2$ with Na/K to give $[\text{Cp}^*\text{Al}]_4$ proceeded in greatest yield when $X = \text{I}$ [14]. We therefore set out to prepare Cp^*ScI_2 (**1**) and study its reaction with chemical reductants under various experimental conditions.

Attempts to prepare **1** directly from ScI_3 and Cp^*M ($\text{M} = \text{Li}, \text{K}, \text{SnBu}_3$) in various solvents gave unsatisfactory results. For example, when ScI_3 and Cp^*Li were heated to 100 °C in benzene- d_6 in a sealed NMR tube a complex reaction mixture resulted. The analogous reaction with Cp^*K cleanly generated Cp^*_2ScI [15]. The reaction of Cp^*SnBu_3 with ScI_3 in benzene- d_6 in the presence THF (2.5 equiv) at 100 °C in a sealed NMR tube yielded the THF adduct of **1**. This reaction required 3 weeks to reach completion, and was thus not further pursued as a route to **1**. Bercaw and coworkers prepared Cp^*ScCl_2 by the chlorination of $\text{Cp}^*\text{Sc}(\text{acac})_2$ ($\text{acac} = \text{acetylacetonate}$) with AlCl_3 [16], and we found this strategy, with minor modifications and using AlI_3 in place of AlCl_3 , to be a successful route to **1**. Compound **1** was prepared in 63% yield (0.88 g) by treatment of $\text{Cp}^*\text{Sc}(\text{acac})_2$ [16] with 2 equiv of AlI_3 in pentane (Eq. (1)). The bright yellow product, which has a single resonance at 2.07 ppm in its ^1H NMR spectrum (in benzene- d_6), was purified by crystallization from toluene at –30 °C. Attempts to prepare **1** on multigram scales resulted in reduced yields.



X-ray quality crystals were obtained by layering a toluene solution of **1** with hexamethyldisiloxane followed by slow cooling to –30 °C. The molecular structure is shown in Fig. 1, and the crystal data is summarized in Table 1. The compound crystallizes in space group $P\bar{1}$, and exists as an inversion-symmetric, cyclic tetramer. The unit cell contains one tetramer and one molecule of hexamethyldisiloxane. The solvent molecule is disordered about an inversion center, and a pair of inversion-related Cp^* ligands are rotationally disordered. As a result, the atoms in these moieties were modeled isotropically, while all other non-hydrogen atoms were modeled anisotropically.

The scandium atoms sit at the corners of a square, with bridging iodides above and below the plane described by the scandium atoms. The geometry about

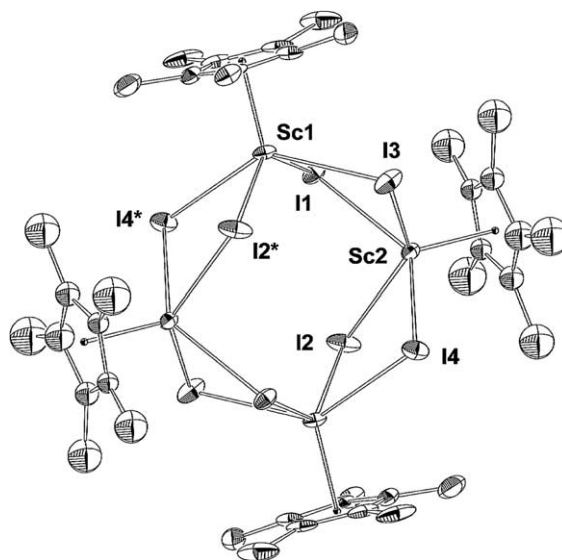


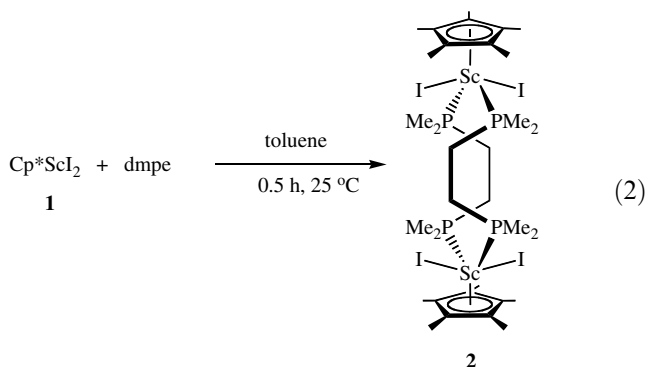
Fig. 1. ORTEP diagram of $[\text{Cp}^*\text{ScI}_2]_4$ (**1**). Thermal ellipsoids are drawn at 50% probability. The hydrogen atoms and the solvent molecule are omitted for clarity. Only one Cp^* orientation is shown for the disordered Cp^* rings. Selected interatomic distances (Å): $\text{Sc}(1)\text{--I}(1) = 2.952(2)$, $\text{Sc}(1)\text{--I}(2) = 2.938(2)$, $\text{Sc}(1)\text{--I}(3) = 2.938(2)$, $\text{Sc}(1)\text{--I}(4)^* = 2.975(2)$, $\text{Sc}(2)\text{--I}(1) = 2.944(2)$, $\text{Sc}(2)\text{--I}(2) = 2.930(2)$, $\text{Sc}(2)\text{--I}(3) = 2.951(2)$, $\text{Sc}(2)\text{--I}(4) = 2.947(2)$, $\text{Sc}(1)\text{--Cp}^*(\text{centroid}) = 2.136(2)$, $\text{Sc}(2)\text{--Cp}^*(\text{centroid}) = 2.159(2)$.

each scandium atom is approximately square pyramidal with the Cp^* centroid in the apical position. The average $\text{Sc}\text{--I}$ bond length observed in **1** is 2.947(1) Å. While there are no organoscandium iodides in the CCDC database with which to compare this value, the averaged bond length observed in **1** is exactly the sum of the anionic radius of I^- and the cationic radius of Sc^{3+} [17]. The average $\text{Cp}^*(\text{centroid})\text{--Sc}$ distance of 2.148(1) Å is slightly shorter than $\text{Cp}^*(\text{centroid})\text{--Sc}$ distances observed in decamethylscandocene complexes (e.g. 2.1705 Å in Cp^*_2ScMe [15], 2.194 Å in $\text{Cp}^*_2\text{Sc}(\eta^2\text{-pyridyl})$ [15], 2.172 Å in $\text{Cp}^*_2\text{Sc}\text{--CC}\text{--ScCp}^*_2$ [18], and 2.1991 and 2.2057 Å in $(\text{Cp}^*_2\text{Sc})_2\text{Se}$ and $(\text{Cp}^*_2\text{Sc})_2\text{Te}$, respectively) [19].

Attempts to prepare phosphine derivatives of **1** were largely unsuccessful. The reactions of **1** with PMe_3 , bis(diphenylphosphino)ethane, and bis(diisopropylphosphino)ethane under various reaction conditions yielded mixtures of unidentified products. Compound **1** did react cleanly with bis(dimethylphosphino)ethane (dmpe) in toluene to precipitate colorless crystals of $[\text{Cp}^*\text{ScI}_2(\mu\text{-dmpe})]_2$ (**2**), isolated in 24% yield (Eq. (2)). X-ray crystallography established the connectivity of the atoms in **2** as the dmpe -bridged dimer shown in Eq. (2), but problems with the data set precluded accurate refinement of metric parameters. Examination of the raw intensity data revealed that the crystal used in the data collection was not single.

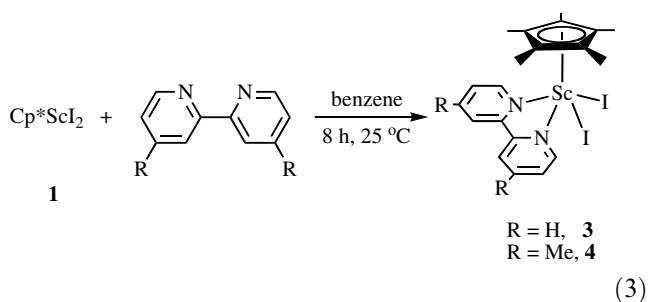
Table 1
Selected crystal data for **1**, **5**, and **7**

	Compound		
	1	5	7
Formula	C ₄₆ H ₇₈ Sc ₄ I ₈ Si ₂ O	C ₈₀ H ₉₂ Sc ₄ N ₈ I ₄	C _{43.5} H ₅₀ Cl ₂ N ₂ Sc ₂
MW (g/mol)	1898.35	1853.12	785.69
Color	Yellow	Black	Black
Crystal habit	Block	Block	Block
Crystal dimensions (mm)	0.16 × 0.25 × 0.19	0.38 × 0.28 × 0.26	0.30 × 0.41 × 0.27
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 1̄ (#2)	<i>P</i> 2 ₁ / <i>c</i> (#14)	<i>C</i> 2/ <i>c</i> (#15)
<i>a</i> (Å)	9.1661(2)	20.004(2)	25.7709(4)
<i>b</i> (Å)	12.6431(3)	19.231(2)	19.62060(10)
<i>c</i> (Å)	14.4952(2)	20.999(2)	18.4253(2)
α (°)	79.814(1)		
β (°)	76.222(1)	109.584(4)	121.441(1)
γ (°)	83.066(1)		
<i>V</i> (Å ³)	1600.33(5)	7610(1)	7948.7(2)
<i>Z</i>	1	4	8
Radiation	Mo K α (λ = 0.71069)	Mo K α (λ = 0.71069)	Mo K α (λ = 0.71069)
Diffraction	SMART	SMART	SMART
Scan type	ω (0.3° per frame)	ω (0.3° per frame)	ω (0.3° per frame)
2 θ_{\max} (°)	49.3	49.6	49.5
Number of reflections collected	Total: 8043 Unique: 5036 (<i>R</i> _{int} = 0.032)	Total: 32,204 Unique: 12,766 (<i>R</i> _{int} = 0.049)	Total: 17,744 Unique: 6820 (<i>R</i> _{int} = 0.050)
Absorption correction	Empirical	Empirical	Empirical
Number of observations (<i>I</i> > 3.00 σ)	3690	7526	3961
Number of variables	263	865	455
Reflections/parameters ratio	14.03	8.70	8.71
<i>R</i>	0.042	0.051	0.049
<i>R</i> _w	0.057	0.062	0.058
<i>R</i> _{all}	0.059	0.082	0.087
Goodness-of-fit	1.42	1.70	1.54



Treatment of **1** with bipyridine in benzene at room temperature afforded Cp*ScI₂(bpy) (**3**) as a bright orange powder in 87% yield (Eq. (3)). The compound precipitated from the reaction mixture and was easily purified by filtration followed by washing with benzene and then pentane. The ¹H NMR spectrum of **3** (in dichloromethane-d₂) contains four resonances for the bipyridine ligand at 7.67 (t, *J* = 6 Hz), 8.12 (t, *J* = 8 Hz), 8.18 (d, *J* = 8 Hz), and 9.75 ppm (d, *J* = 6 Hz), each integrating to 2H, and a singlet resonance at 1.88 ppm integrating to 15H for the Cp* ligand. While **1** decomposed to a white solid within

seconds of exposure to air, **3** reacted much more slowly with air and samples remained unchanged even after several hours in the air.



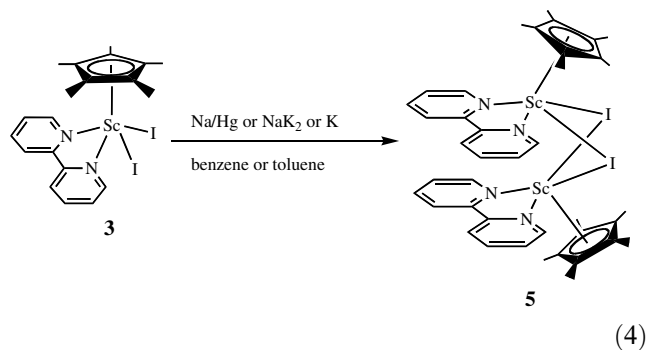
The 4,4'-dimethyl-2,2'-bipyridine (dmb) adduct of **1**, Cp*ScI₂(dmb) (**4**), was prepared in an analogous manner, and was isolated as a bright yellow powder in 53% yield (Eq. (3)). Elemental analysis and ¹H NMR spectroscopy confirmed the presence of 1/8 equiv of benzene, which could not be removed under vacuum. Subsequent preparations of the compound also contained 1/8 equiv of benzene. The ¹H NMR spectrum of **4** in dichloromethane-d₂ contains two singlet resonances at 1.88 (15H) and 2.56 ppm (6H) corresponding to the methyl groups on the Cp* and dmb ligands, respectively. The

expected dmb aromatic resonances were observed at 7.46, 7.97, and 9.54 ppm, as was a singlet resonance at 7.35 ppm integrating to 0.75H and corresponding to the 1/8 equiv of benzene.

2.2. Reduction of scandium(III) precursors

Reactions of **1** with various reducing agents (Na amalgam, NaK₂, KC₈, K metal, etc.) under a range of conditions were explored. In all cases **1** was consumed, but attempts to characterize the reaction products were unsuccessful. Attempts to isolate and characterize the products of reactions of **2** with these reductants were also unsuccessful.

In contrast to these results, **3** reacted with various reducing agents (0.1% Na amalgam, NaK₂, and K metal) in aromatic solvents to yield [Cp*ScI(bpy)]₂ (**5**) (Eq. (4)), a compound which has been characterized by ¹H NMR and infrared spectroscopies, elemental analysis, and X-ray crystallography. The most convenient preparation of **5** involves stirring **3** with NaK₂ (2 equiv) in toluene at room temperature for 10 days. Large black crystals of **5** (22% yield) were obtained by filtration of the reaction mixture, followed by concentration in vacuo and cooling to –35 °C.



The ¹H NMR spectrum of **5** in benzene-d₆ contains a resonance at 1.98 ppm (s, 15H) for the Cp* ligand, and resonances at 5.41 (d, 2H, *J* = 8.8 Hz), 5.90 (br s, 2H), 6.24 (br s, 2H), and 7.42 (d, 2H, *J* = 6.4 Hz) for the bipyridine ligand. The bipyridine resonances are shifted significantly upfield from the values observed for **3** and for free bipyridine, and this is consistent with the ligand being in a more electron-rich environment.

The infrared spectrum of **5** contains a sharp peak at 963 cm⁻¹. It has been noted that the bipyridine radical anion, when coordinated to a metal center, absorbs strongly in the region 900–1000 cm⁻¹ [20,21]. No absorption in this region is observed for **3**. Furthermore, a strong absorption around 1600 cm⁻¹ is expected for a neutral bipyridine ligand but such a peak is absent from the spectrum of **5**. Note that, as expected, **3** exhibits this absorption at 1598 cm⁻¹. These data suggest that the bipyridine ligand in **5** is best described as a bipyridyl radical anion.

The UV/vis spectra of bipyridine, the bipyridine radical anion, and the bipyridine dianion have been extensively studied [20,22–24] and have been shown to differ significantly from one another. While neutral bipyridine does not absorb in the visible region, the optical spectra of Na(bpy) and Na₂(bpy) contain absorbances at 816 and 531 nm, and 610 and 373 nm, respectively [24]; (see Table 2). For **5** in toluene, absorbances were observed at 808, 506 (sh), 384, and 304 nm. These data, particularly the presence of an absorbance around 800 nm and the lack of one near 600 nm, are most consistent with formulation of the bipyridine ligand as a radical anion.

The structure of **5** was determined by X-ray crystallography. X-ray quality crystals were obtained by layering a toluene solution of **5** with pentane, and allowing the layers to slowly diffuse together at –30 °C over several days. The compound crystallized in space group *P2₁/n* with two independent molecules in the asymmetric unit. No significant differences were observed between the two independent molecules.

As shown in Fig. 2, **5** has a dimeric structure in which the two scandium centers are bridged by the two iodide ligands. A Cp* and a bipyridine ligand complete the coordination sphere of each scandium. Each scandium center is thus in a square pyramidal coordination environment with the Cp* centroid occupying the apical position. The two bipyridine ligands are arranged in a *cis* orientation and are coplanar. A search of the CCDC database revealed numerous dimeric complexes in which two bipyridine ligands are coordinated to two transition metal centers that are bridged by two single-atom bridges, but in all but a few examples Rh₂(η¹-C₆H₅S)₂(μ-C₆H₅S)₂(bpy)₂ and [Cp*W(R₂bpy)(μ-O)]₂[PF₆]_n (R₂bpy = 4,4'-R,R-2,2'-bipyridine; R = NMe₂, *t*Bu, Me; *n* = 0, 1, 2, 3) [25,26] the bipyridine ligands are in a *trans* orientation.

The average Sc–I bond length in **5** (2.998(1) Å) is slightly longer than that observed in **1** (2.947(1) Å). At 2.164 Å, the average Cp*(centroid)–Sc bond distance of **5** is also longer than that observed in **1**, but still shorter than those typically observed in decamethylscandocene complexes. While a scandium(II) center is expected to have a larger ionic radius than a scandium(III) center and thus make longer bonds to most ligands, the lengthening observed on going from **1** to **5** is probably not enough to argue convincingly for a reduced scandium

Table 2
Optical data for **5** and reference compounds [24] in toluene

Compound	λ_{max} in nm ($\epsilon \times 10^{-3}$ in L · mol ⁻¹ cm ⁻¹)
5	808 (1.4), 506 (2.1), 384 (7.0), 304 (17)
bpy	237 (12.2), 283 (14.5)
Na(bpy)	816 (1.5), 531 (1.7), 385 (4.4)
Na ₂ (bpy)	610 (1.7), 373 (9.9), 325 (1.2)

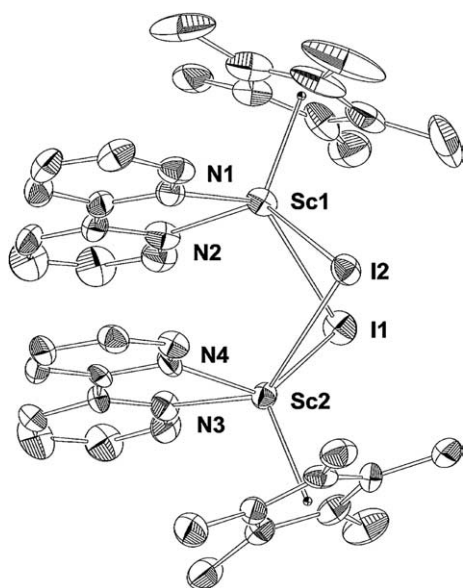


Fig. 2. ORTEP diagram of $[\text{Cp}^*\text{ScI}(\text{bpy})]_2$ (**5**). Thermal ellipsoids are drawn at 50% probability. The hydrogen are omitted for clarity. Only one molecule of **5** is depicted. Selected interatomic distances (Å): Sc(1)–I(1) = 3.021(2), Sc(1)–I(2) = 2.976(2), Sc(2)–I(1) = 2.987(2), Sc(2)–I(2) = 3.006(2), Sc(1)–N(1) = 2.182(9), Sc(1)–N(2) = 2.196(9), Sc(2)–N(3) = 2.234(9), Sc(2)–N(4) = 2.194(9), Sc(1)–Cp*(centroid) = 2.162(2), Sc(2)–Cp*(centroid) = 2.161(2).

center, especially in light of the crystallographic evidence for a reduced bipyridine ligand (vide infra).

Addition of an electron to the LUMO of bipyridine should result in predicted changes in the bond lengths of the ligand. For example, the central C–C bond of the ligand is expected to shorten upon reduction [27]. The C–C and C–N bond lengths of the bipyridine ligand in **5** compare much more favorably with those observed in bipyridine radical anions than with those observed for neutral bipyridine ligands coordinated to metals (Fig. 3, Table 3) [7,20]. For example, the average inter-ring C–C bond length in **5** is 1.45(1) Å, which may be compared to

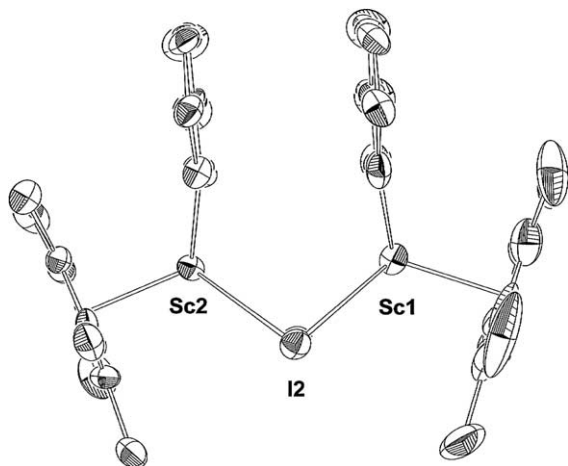


Fig. 3. Side view of $[\text{Cp}^*\text{ScI}(\text{bpy})]_2$ (**5**).

a value of 1.490(3) Å for free bipyridine [28], and to 1.434 Å in $\text{Cp}^*\text{Yb}(\text{bpy})$ [20] and 1.416 Å in $[\eta^5, \eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{NMe}_2]\text{Sc}(\text{dmb})_2$ [7] – compounds known to contain bipyridine radical anions.

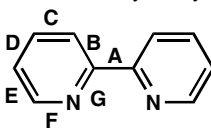
As noted above, the two bipyridine ligands in **5** are arranged in a coplanar, *cis* orientation with, on average, a distance of 3.30 Å between corresponding atoms (the closest contact is 3.19 Å for N1–N3; the longest is 3.47 Å for C58–C73). The average distance between an atom in one bipyridine ligand and the least-squares plane defined by the atoms of the other bipyridine ligand is 3.29 Å. The angle between least-squares planes defined by the atoms in the bipyridine ligands is 3.1° in one molecule (containing Sc1 and Sc2) and 3.0° in the other (containing Sc3 and Sc4). That the bipyridine ligands are nearly parallel and so close together is remarkable, especially since the Sc–Sc separation in the molecule is 3.66–3.69 Å, i.e., the bipyridine ligands are actually closer to one another than the scandium atoms to which they are coordinated (see Fig. 3). The bipyridine–bipyridine separation is smaller than the inter-layer distance in graphite (3.35 Å) [29] and is suggestive of a significant π – π interaction between these ligands. The average distance between a bipyridine ligand and the Cp* methyl carbon atoms directly above it is 3.21 Å.

The structure observed in **5** can be compared to those of $[\text{Cp}^*\text{W}(\text{R}_2\text{bpy})(\mu\text{-O})]_2[\text{PF}_6]_n$ ($\text{R}_2\text{bpy} = 4,4'\text{-R,R-2,2'}$ -bipyridine; R = NMe₂, *t*Bu, Me; *n* = 0, 1, 2, 3) prepared by Cremer and Burger [26]. In all but one case (R = Me, *n* = 0), the bipyridine ligands are arranged in a *cis* orientation, as in **5**. In all of these molecules there is some degree of W–W bonding, and thus the metal–metal distances observed (2.69–2.76 Å) are uniformly shorter than that in **5**. For those with a *cis* arrangement of bipyridine ligands, the closest inter-ligand contact (3.06–3.15 Å) is greater than the W–W distance, in contrast to the situation observed for **5**. Furthermore, while the bipyridine ligands in **5** are nearly co-planar, in the tungsten complexes the bipyridine ligands are distinctly non-coplanar. In all of these complexes, corresponding atoms in the bipyridine ligands nearest to the W₂O₂ ring are 0.7–1.4 Å closer together than those farthest away.

The infrared and UV/vis spectroscopic data in conjunction with the crystal structure of **5** suggest that the bipyridine ligands of the molecule are reduced to radical anions. A ¹H NMR spectrum could be observed in a window typical for diamagnetic compounds, and no magnetic moment could be detected by the Evans' method [30]. This suggests that there is a strong coupling between the single electrons localized on the bipyridine ligands, and the close proximity of these ligands observed in the crystal structure corroborates this hypothesis. A more detailed study of the magnetic properties of **5** and theoretical calculations would be useful in further characterizing the electronic structure of this molecule.

Table 3

Bond distances (Å) in bipyridine and bipyridine complexes as determined by X-ray crystallography

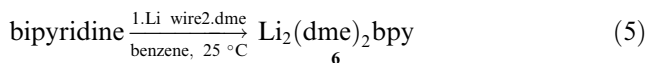


Compound	A	B	C	D	E	F	G
5	1.45(1)	1.42(1)	1.36(1)	1.40(1)	1.36(1)	1.37(1)	1.38(1)
6	1.418(5)	1.408(3)	1.362(4)	1.406(4)	1.367(4)	1.350(4)	1.387(4)
Bipyridine	1.490	1.394	1.385	1.383	1.384	1.341	1.346
Cp* ₂ Y(bpy)	1.434	1.419	1.387	1.420	1.398	1.358	1.383
[η ⁵ ,η ¹ -C ₅ H ₄ (CH ₂) ₂ NMe ₂]Sc(dmb) ₂	1.416	1.403	1.353	1.396	1.348	1.352	1.373

Labelling scheme for bipyridine.

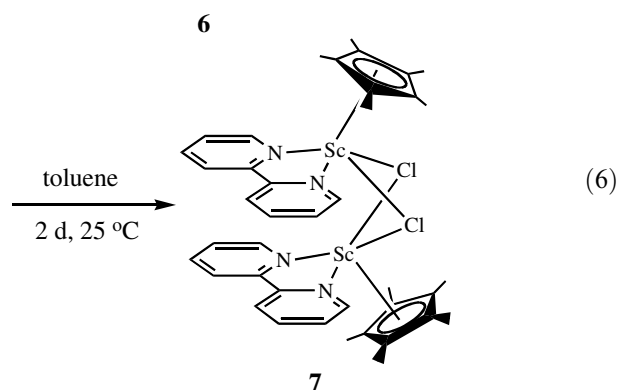
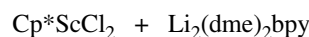
Compound **5** can be heated for at least one week to 100 °C in benzene-d₆ in a sealed NMR tube without noticeable changes in its ¹H NMR spectrum. The reaction of **5** with I₂ in toluene at –30 °C yielded an insoluble brown powder. The ¹H NMR spectrum of this powder in dichloromethane-d₂ contained resonances for **3** as well as resonances for unidentified products. Attempts to cleanly reduce **5** with excess NaK₂ or K metal gave no reaction, while reaction with KC₈ consumed the starting material, but produced several unidentified products.

In an attempt to prepare [Cp*Sc(bpy)], the reaction of **1** with the bipyridine dianion Li₂(dme)₂bpy (dme = dimethoxyethane) (**6**) was examined. Compound **6** was prepared in 60% yield by stirring bipyridine and Li wire (2.8 equiv) in benzene under argon at room temperature (Eq. (5)). After 18 h, the mixture was deep purple and excess dme was added. After an additional two days at room temperature, the reaction mixture was filtered to remove excess lithium wire, and the solvent and excess dme were removed in vacuo affording **6** as deep red crystals that could be stored indefinitely in an inert atmosphere. The ¹H NMR spectrum of **6** in benzene-d₆ contains only two broad resonances that appear at different chemical shifts depending on the sample concentration. When ¹H NMR samples of **6** were quenched by exposure to air, resonances corresponding to free bipyridine and 2 equiv of dme were observed. Samples of **6** give satisfactory elemental analysis.



The reaction of **6** with **1** in benzene at room temperature yielded **5** rather than the halide-free Cp*Sc(bpy) complex. This result suggested that the chloride analog of **5**, [Cp*ScCl(bpy)]₂ (**7**), might also be obtained by this route, and indeed this proved to be the case. Equimolar quantities of **6** and Cp*ScCl₂ [16] were stirred in toluene for 2 days at room temperature. The volatile reaction components were removed in vacuo (in order to remove dme) leaving a black mass that was extracted with toluene.

The toluene extract was then filtered, concentrated, and stored at –30 °C for several days to afford **7** as black crystals in 20% yield (Eq. (6)).



The Cp* resonance of **7** in benzene-d₆ appears at 1.99 pm in the ¹H NMR spectrum. This chemical shift is almost identical to the corresponding value observed for **5**. The ¹H NMR spectrum also contains resonances for 0.5 equiv of toluene. Elemental analysis and X-ray crystallography confirm that toluene is present in this amount. Interestingly, only one of the four expected bipyridyl resonances is observed: a doublet (*J* = 9.6 Hz) at 5.46 ppm.

The infrared spectrum of **7** closely resembles that of **5**, and suggests bipyridyl radical anion character; it contains a strong absorbance at 968 cm^{–1} but lacks one near 1600 cm^{–1}.

Crystals of **7** suitable for X-ray crystallography were obtained by layering a toluene solution of **7** with pentane and storing for several days at –35 °C. The compound crystallized in the space group *C*₂/*c* with one molecule of **7** and one half molecule of toluene in the asymmetric unit. All non-hydrogen atoms were modeled anisotropically except the carbon atoms (C41–C46) of the very disordered toluene molecule.

The structure of **7** (Fig. 4) is analogous to that of **5**. Each scandium atom is in a square pyramidal coordina-

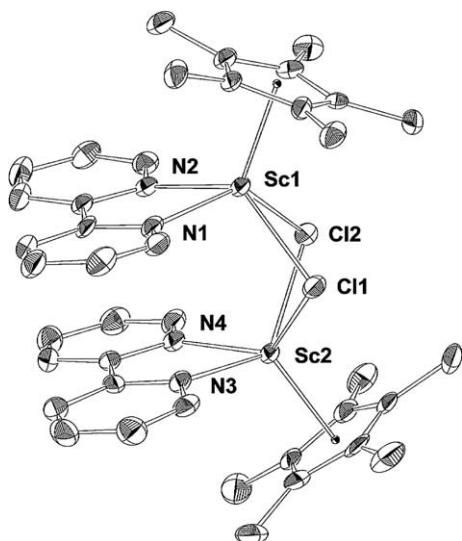


Fig. 4. ORTEP diagram of $[\text{Cp}^*\text{ScCl}(\text{bpy})]_2$ (**7**). Thermal ellipsoids are drawn at 50% probability. The hydrogen atoms and the solvent molecule are omitted for clarity. Selected interatomic distances (Å): Sc(1)–Cl(1) = 2.573(1), Sc(1)–Cl(2) = 2.574(1), Sc(2)–Cl(1) = 2.565(1), Sc(2)–Cl(2) = 2.585(2), Sc(1)–N(1) = 2.194(4), Sc(1)–N(2) = 2.205(4), Sc(2)–N(3) = 2.201(4), Sc(2)–N(4) = 2.188(4), Sc(1)–Cp*(centroid) = 2.1547(9), Sc(2)–Cp*(centroid) = 2.1479(8).

tion environment, including the Cp* centroid, a bipyridine ligand, and two chloride ligands. The two chloride ligands bridge the scandium centers and the two bipyridine ligands are arranged co-facially in a *cis* orientation, as in **5**.

The average Sc–Cl bond distance in **7** (2.574(1) Å) is within the range observed for other molecules containing Sc_2Cl_2 units. For example, the Sc–Cl bond distances in $[\text{Cp}_2\text{ScCl}]_2$ range from 2.565 to 2.584 Å [31]. The average Cp*(centroid)–Sc distance in **7** is 2.151 Å – longer than observed in **1**, but shorter than that observed in **5** and in decamethylscandocene complexes. As was observed for **5**, the C–N and C–C bond distances in **7** compare most favorably with those observed in bipyridine radical anion species (Table 3).

The Sc–Sc separation in **7** (3.393(1) Å) is shorter than that observed for **5** (3.66–3.69 Å), which is not surprising given the smaller ionic radius of chloride (vs. iodide). As observed for **5**, the bipyridine ligands in **7** are nearly planar (Fig. 5), with the angle between least-squares planes defined by the bipyridine ligands being 3.8°. The average separation between an atom in one bipyridine ligand and the least squares plane defined by the other bipyridine ligand is 3.29 Å, which is shorter than the Sc–Sc separation in the molecule and shorter than the interplane distance in graphite. The average separation between a bipyridine ligand and the Cp* methyl carbon atoms directly above it is 3.23 Å. The crystallographic and spectroscopic data for **7** suggest significant radical anion character for the bipyridines and a strong

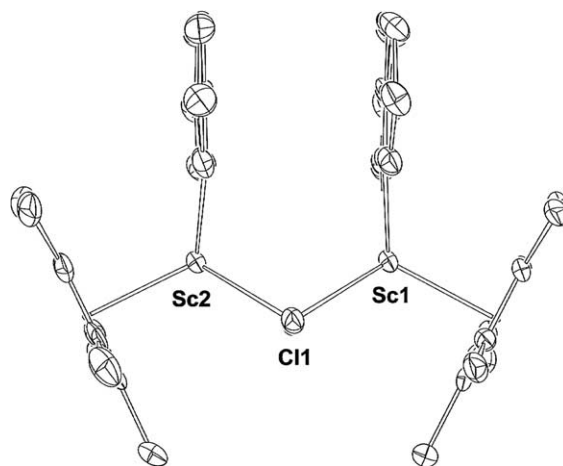


Fig. 5. Side view of $[\text{Cp}^*\text{ScCl}(\text{bpy})]_2$ (**7**).

magnetic coupling between the unpaired electrons on the two ligands.

When $\text{Cp}^*\text{ScI}_2(\text{dmb})$ (**4**) was subjected to reductants and conditions that successfully reduced **5** and **7**, no reaction products could be isolated or characterized. Perhaps the extra steric bulk of the methyl groups on the dimethylbipyridine ligands preclude the formation of a stable, reduced dimer analogous to **5** or **7**.

3. Concluding remarks

In an effort to expand the number of known low-valent organoscandium compounds, we have prepared molecules containing $\text{Sc}_2^{+3}(\text{bpy}^-)_2$ fragments that exhibit significant interactions between the bipyridine ligands. To the best of our knowledge **5** and **7** are the first crystallographically characterized complexes containing reduced bipyridine ligands arranged in a co-facial manner. Studies are underway to further characterize the magnetic properties of these molecules in order to better understand the interaction between the bipyridine ligands. The precursor to **5** and **7**, Cp^*ScI_2 (**1**) is an addition to the small but growing number of lanthanide cluster compounds bearing Cp-type ligands [32].

4. Experimental procedures

4.1. General procedures

All experiments were conducted under a nitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres drybox unless otherwise noted. Dry, oxygen free solvents were used unless otherwise noted. Olefin impurities were removed from pentane by treatment with concentrated H_2SO_4 , 0.5 M KMnO_4 in 3 M H_2SO_4 , and saturated NaHSO_4 . Pentane was

then dried over MgSO_4 , stored over activated 4 Å molecular sieves, and distilled from potassium benzophenone ketyl under a nitrogen atmosphere. Thiophene impurities were removed from toluene and benzene by treatment with H_2SO_4 and then saturated NaHCO_3 . These solvents were then dried over MgSO_4 and distilled from potassium under a nitrogen atmosphere. Benzene- d_6 was degassed by three freeze–pump–thaw cycles and dried for several days over activated 4 Å molecular sieves. Methylene chloride- d_2 was purified by vacuum distillation from calcium hydride.

NMR spectra were recorded at 400.134 MHz (^1H) and 100.614 MHz (^{13}C) using a Bruker AVB-400 spectrometer. ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra were referenced internally by the residual solvent signal relative to tetramethylsilane. All spectra were recorded at room temperature. Infrared spectra were recorded as KBr pellets using a Mattson FTIR spectrometer at a resolution of 4 cm^{-1} . Elemental analyses were performed by the College of Chemistry Microanalytical Laboratory at the University of California, Berkeley.

All chemicals were obtained from Aldrich or Cerac and used as received, except for AlI_3 which was purified by the following procedure: Iodine was removed from technical grade AlI_3 in vacuo at room temperature. The iodine-free AlI_3 was then purified by sublimation in vacuo at 130°C .

4.2. Synthesis of Cp^*ScI_2 (1)

Pentane (40 ml) was added via cannula to a Schlenk tube containing $\text{Cp}^*\text{Sc}(\text{acac})_2$ (1.21 g, 3.20 mmol) and AlI_3 (2.62 g, 6.42 mmol). The resulting slurry was stirred for 8 h, during which time a bright yellow color developed. The supernatant was removed via cannula filtration, and the yellow precipitate was washed with pentane ($3 \times 20\text{ ml}$). The precipitate was then recrystallized from toluene at -30°C to yield analytically pure **1** (0.88 g, 63%). M.p.: $158\text{--}165^\circ\text{C}$ dec. ^1H NMR (benzene- d_6): δ 2.07 (s). ^1H NMR (THF- d_8): δ 2.19 (s). ^1H NMR (methylene chloride- d_2): δ 2.26 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6): δ 14.97, 112.72. IR (KBr, cm^{-1}): 1023 (m), 1378 (s), 1428 (s), 1489 (m), 1534 (m), 1602 (m), 2730 (w), 2906 (s), 2939 (m), 2974 (m). Anal. Calc. for $\text{C}_{10}\text{H}_{15}\text{I}_2\text{Sc}$: C, 27.68; H, 3.48. Found: C, 27.61; H, 3.47%.

4.3. Synthesis of $[\text{Cp}^*\text{ScI}_2(\mu\text{-dmpe})]_2$ (2)

A solution of dmpe (64 μl , 0.38 mmol) in toluene (2 ml) was added via cannula to a yellow solution of **1** (0.162 g, 0.37 mmol) in toluene (10 ml). The solution immediately became colorless, and a white solid precipitated. The supernatant was removed via cannula filtration, and the product was washed with toluene (5 ml) and pentane (10 ml) and dried in vacuo for 18 h. (yield:

0.053 g, 24%). M.p.: $227\text{--}232^\circ\text{C}$ dec. IR (KBr, cm^{-1}): 728 (m), 889 (m), 939 (s), 1022 (w), 1281 (m), 1293 (m), 1374 (w), 1419 (m), 1448 (w), 2722 (w), 2905 (s), 2970 (m). Anal. Calc. for $\text{C}_{32}\text{H}_{64}\text{I}_4\text{P}_4\text{Sc}_2$: C, 32.90; H, 5.35. Found: C, 32.71; H, 5.16%.

4.4. Synthesis of $\text{Cp}^*\text{ScI}_2(\text{bpy})$ (3)

Benzene (15 ml) was added to solid Cp^*ScI_2 (0.40 g, 0.92 mmol) and bipyridine (0.15 g, 0.94 mmol) to give a yellow slurry which was stirred for 8 h. The reaction mixture was then filtered to give an orange solid that was washed with benzene (10 ml) and pentane ($2 \times 20\text{ ml}$). Residual solvent was removed in vacuo, to afford **3** as a bright orange powder (0.48 g, 87%). ^1H NMR (methylene chloride- d_2): δ 1.88 (s, 15H, C_5Me_5), 7.67 (t, 2H, $J = 6\text{ Hz}$, bpy), 8.12 (t, 2H, $J = 8\text{ Hz}$, bpy), 8.18 (d, 2H, $J = 8\text{ Hz}$, bpy), 9.75 (d, 2H, $J = 6\text{ Hz}$, bpy). IR (KBr, cm^{-1}): 426 (m), 631 (w), 650 (m), 734 (m), 761 (s), 1018 (s), 1063 (m), 1103 (w), 1156 (m), 1175 (w), 1315 (m), 1377 (m), 1436 (s), 1473 (s), 1493 (m), 1563 (m), 1598 (s), 1698 (vw), 1773 (vw), 1867 (vw), 1969 (vw), 1991 (vw), 2725 (w), 2855 (m), 2903 (s), 2944 (m), 2967 (m), 3030 (w), 3053 (w), 3072 (w), 3108 (w). Anal. Calc. for $\text{C}_{20}\text{H}_{23}\text{I}_2\text{N}_2\text{Sc}$: C, 40.70; H, 3.93; N, 4.75. Found: C, 40.57; H, 3.77; N, 4.91%.

4.5. Synthesis of $\text{Cp}^*\text{ScI}_2(\text{dmb})$ $1/8\text{C}_6\text{H}_6$ (4)

Benzene (8 ml) was added to solid Cp^*ScI_2 (0.14 g, 0.32 mmol) and dimethylbipyridine (0.06 g, 0.34 mmol) to give a yellow slurry which was stirred for 8 h at room temperature. The reaction mixture was then filtered to give a yellow solid that was washed with benzene ($2 \times 5\text{ ml}$) and pentane (5 ml). Residual solvent was removed in vacuo, to afford **4** as a bright yellow powder (0.10 g, 53%). ^1H NMR (methylene chloride- d_2): δ 1.88 (s, 15H, C_5Me_5), 2.56 (s, 6H, $\text{Me}_2\text{-bpy}$), 7.35 (s, 0.75H, $1/8\text{C}_6\text{H}_6$), 7.46 (d, 2H, $J = 5.6\text{ Hz}$, bpy), 7.97 (s, 2H, bpy), 9.54 (d, 2H, $J = 5.6\text{ Hz}$, bpy). $^{13}\text{C}\{^1\text{H}\}$ NMR (methylene chloride- d_2): δ 32.8, 109.2, 143.2, 208.3, 209.6. IR (KBr, cm^{-1}): Anal. Calc. for: $\text{C}_{22.75}\text{H}_{27.75}\text{I}_2\text{N}_2\text{Sc}$: C, 43.51; H, 4.45; N, 4.46. Found: C, 43.87; H, 4.48; N, 4.29%.

4.6. Synthesis of $[\text{Cp}^*\text{ScI}(\text{bpy})]_2$ (5)

A slurry of $\text{Cp}^*\text{ScI}_2(\text{bpy})$ (0.27 g, 0.45 mmol) in toluene (10 ml) was cannula transferred onto NaK_2 (prepared from 0.008 g Na and 0.023 g K) and the resulting mixture was stirred vigorously at room temperature. The reaction mixture gradually changed from an orange slurry to an opaque black solution. After 10 days the reaction mixture was filtered, and the filtrate was concentrated in vacuo. Cooling the filtrate to -35°C for several days afforded **5** as black crystals (0.047 g,

22%). ^1H NMR (benzene- d_6): δ 1.98 (s, 15H, C_5Me_5), 5.41 (d, 2H, $J = 8.8$ Hz, bpy), 5.90 (br s, 2H, bpy), 6.24 (br s, 2H, bpy), 7.42 (d, 2H, $J = 6.4$ Hz, bpy). IR (KBr, cm^{-1}): 425 (m), 455 (w), 613 (w), 649 (m), 724 (s), 750 (s), 963 (s), 1024 (w), 1089 (m), 1156 (s), 1235 (m), 1278 (m), 1297 (w), 1340 (s), 1375 (m), 1409 (s), 1432 (s), 1456 (w), 1517 (s), 1566 (m), 1670 (w), 1773 (w), 1875 (w), 2310 (vw), 2366 (vw), 2553 (w), 2724 (w), 2854 (m), 2900 (s), 3052 (w), 3144 (w). Anal. Calc. for $\text{C}_{40}\text{H}_{46}\text{I}_2\text{N}_4\text{Sc}_2$: C, 51.85; H, 5.00; N, 6.05. Found: C, 52.21; H, 5.06; N, 5.93%. M.p.: 274–276 °C.

4.7. Synthesis of $\text{Li}_2\text{bpy}(\text{dme})_2$ (**6**)

Against an argon counter flow, lithium wire (1.4 cm of 45 mg/cm wire, 9.1 mmol) was added to a Schlenk flask containing a solution of bipyridine (0.51 g, 3.3 mmol) in benzene (15 ml). The mixture was stirred vigorously and a deep purple color developed quickly. After stirring for 18 h, DME (5 ml) was added, and the reaction mixture was allowed to stir for two more days. The red/brown reaction mixture was then filtered and the solvent was removed in vacuo to yield **6** as deep red crystals (0.69 g, 60%). IR (KBr, cm^{-1}): 435 (w), 504 (br m), 626 (m), 713 (w), 869 (m), 947 (m), 960 (m), 1007 (m), 1080 (s), 1109 (m), 1123 (m), 1139 (m), 1270 (s), 1412 (m), 1432 (s), 1456 (s), 1480 (s), 1502 (m), 1590 (w), 1671 (vw), 1856 (vw), 2428 (vw), 2534 (vw), 2613 (vw), 2687 (vw), 2766 (w), 2828 (m), 2934 (m), 2991 (m), 3057 (m), 3109 (w). Anal. Calc. for: $\text{C}_{18}\text{H}_{28}\text{Li}_2\text{N}_2\text{O}_4$: C, 61.72; H, 8.06; N, 8.00. Found: C, 61.72; H, 7.93; N, 8.35%.

4.8. Synthesis of $[\text{Cp}^*\text{ScCl}(\text{bpy})_2]\text{I}_2(\text{C}_7\text{H}_8)$ (**7**)

Toluene (10 ml) was added to a flask containing Cp^*ScCl_2 (0.202 g, 0.803 mmol) and $\text{Li}_2\text{bpy}(\text{dme})_2$ (0.210 g, 0.807 mmol) and the resulting deep red solution was stirred for 2 days at room temperature. The volatile components of the reaction mixture were then removed in vacuo, and the black mass that remained was extracted with toluene (15 ml). The toluene extract was filtered and its volume reduced to 12 ml in vacuo. The product was obtained as black crystals (0.052 g, 20%) by layering the filtrate with pentane (10 ml) and storing at -30 °C for 10 days. ^1H NMR (benzene- d_6): δ 1.99 (s, 15H, C_5Me_5), 2.10 (s, 0.8H, *Me Ph*), 5.46 (d, 2H, $J = 9.6$ Hz, bpy), 7.02 (m, 1.3H, *Me Ph*). IR (KBr, cm^{-1}): 423 (m), 613 (w), 651 (m), 726 (s), 752 (m), 968 (s), 1012 (m), 1025 (m), 1089 (m), 1156 (s), 1236 (m), 1260 (w), 1285 (m), 1339 (s), 1375 (m), 1411 (s), 1434 (s), 1495 (w), 1515 (m), 1565 (m), 1601 (w), 1670 (w), 1773 (vw), 1876 (vw), 2362 (vw), 2562 (w), 2724 (w), 2857 (m), 2905 (s), 3054 (w), 3140 (vw). Anal. Calc. for: $\text{C}_{43.5}\text{H}_{50}\text{Cl}_2\text{N}_4\text{Sc}_2$: C, 66.16; H, 6.38; N, 7.09. Found: C, 66.06; H, 6.41; N, 7.28%.

4.9. Structure determinations

In all cases, a crystal suitable for X-ray diffraction was mounted on a glass fiber using Paratone N hydrocarbon oil. X-ray measurements were made on a Siemens SMART diffractometer with a CCD area detector, using graphite-monochromated Mo $\text{K}\alpha$ radiation. A hemisphere of data was collected using ω scans of 0.3° and 10 s frames. The frame data were integrated using the program SAINT [33]. An empirical absorption correction based on the measurements of multiply redundant data was applied using the program SADABS [34]. Equivalent reflections were merged, and the data were corrected for Lorentz and polarization effects. Structures were solved using the teXsan crystallographic software package of the Molecular Structure Corporation, using direct methods (SIR92), and expanded with Fourier techniques. Structures were refined as described in the text. In all cases, the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weighting scheme was based on counting statistics and included a p -factor to down-weight intense reflections. Crystallographic data are summarized in Table 1.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre CCDC No. 247735 for compound **1**, No. 247736 for compound **2**, and No. 247737 for compound **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; deposit@ccdc.cam.ac.uk or www.ccdc.ac.uk).

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