

Bridging (Thionylimido)metal Complexes

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ABSTRACT: We report the first examples of the thionylimido ligand acting as a μ_2 -bridging ligand between two transition-metal centers; using $\text{Cp}_2\text{Ti}(\text{NSO})_2$, we describe bi- and tetrametallic systems.

Sulfur–nitrogen transition-metal complexes have attracted many investigations in the past, and while bridging sulfur–nitrogen ligands are not unknown, they are relatively uncommon;¹ complexes containing naked anions displaying different bridging modes, via nitrogen, sulfur, or both, have been reported.^{2–4} (Thionylimido)metal complexes were first reported in the 1980s.¹ To date, there are no examples of $[\text{NSO}]^-$ bridging between transition-metal centers; there are reports of a chromium complex⁶ where the $[\text{NSO}]^-$ anion coordinates to BF_3 as well as the metal and of Me_3SiNSO coordinated to GaCl_3 .⁵ In related work, there has been a report on the formation of bimetallic systems using the tetraimido $[\text{S}(\text{N}t\text{Bu})_4]^{2-}$ anion (an analogue of sulfate).⁷ We note that the $[\text{NSO}]^-$ anion can be considered as an isoelectronic analogue of SO_2 , which has diverse coordination chemistry, including acting as a bridging ligand.⁸ Following our recent work leading to a simplified route to thionylimido complexes,⁹ we decided to investigate the potential for forming bimetallic systems containing the NSO anion. There are a number of examples of bimetallic complexes containing titanium,^{10–14} and together with the report of the use of Cp_2Ti in the bimetallic $[\text{Cp}_2\text{TiNi}(\text{S}_2\text{N}_2)_2]$,¹⁵ this encouraged us to investigate syntheses using bis(thionylimido)titanocene as a scaffold to create heterobimetallic systems. Here we report the first examples of $[\text{NSO}]^-$ -bridged bimetallic TiMo and TiCu and tetrametallic Ti_2Cu_2 complexes.

We first examined the reaction of $\text{Cp}_2\text{Ti}(\text{NSO})_2$ (**1**) with (norbornadiene) $\text{Mo}(\text{CO})_4$ in dichloromethane (DCM). After the addition of **1**, a color change from yellow to purple was observed, although after 1 h of reaction, only a small proportion of the starting materials had reacted by NMR. We found that the reaction is far faster in a mixed solvent system (1:4 ratio of tetrahydrofuran/DCM), enabling the reaction to complete in 5 h rather than over several days in DCM alone. The bimetallic compound **2** was isolated in good yield as a dark-purple solid by precipitation with hexane, and material collected in this way gave satisfactory elemental analysis without further purification. Crystals of **2** suitable for single-crystal X-ray diffraction were grown by cooling a saturated DCM solution of **2**. The structure showed coordination to both metal centers via the nitrogen atoms to create a four-membered ring (Figure 1).

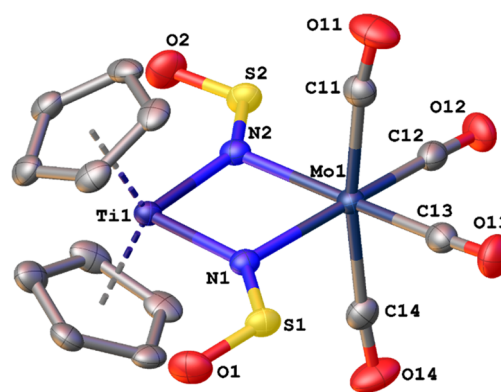


Figure 1. Thermal ellipsoid plot (50% probability ellipsoids) of **2**. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti1–Mo1 3.2083(7), Ti1–N1 2.049(2), Ti1–N2 2.050(2), Mo1–N1 2.263(2), Mo–N2 2.269(2), N1–S1 1.509(2), S2–N2 1.509(2), S1–O1 1.460(2), S2–O2 1.458(2); N1–S1–O1 116.49(13), N2–S2–O2 116.82(13), N1–Ti1–N2 89.24(9), N1–Mo1–N2 78.91(8), Ti1–N1–Mo1 96.02(9), Ti1–N2–Mo1 95.82(9). For comparison in **1**:¹⁶ Ti–N 2.013(2), N–S 1.474(2), S–O 1.452(3); N–S–O 119.1(2) N–Ti–N 96.0(1).

The formation of this ring leads to minor changes from the structure of **1**, the most notable being contraction of the N–Ti–N angle from 96.0(1)° in **1**¹⁶ to 89.24(9)° in **2** and the increase of the Ti–N distance from 2.013(2) Å in **1**⁹ to an average of 2.0495(30) Å in **2**. The N–S–O angles in **2** are somewhat reduced at 116.49(13) and 116.82(13)° compared to those in **1** [119.1(2)°] and $\text{Pt}(\text{PMe}_3)_2(\text{NSO})_2$ [123.3(8) and 121.4(8)°].¹⁶ Further crystallographic data can be found in Table S2.

The ¹H and ¹³C NMR spectra of **2** have only minor changes from those of **1**. The ¹H NMR spectrum gave the expected singlet at 6.22 ppm (cf. 6.37 ppm for **1**),¹⁶ while ¹³C NMR showed the three expected resonances at 115.8 (cf.

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Scheme 1. Synthesis of Bridging Thionylimido Complexes

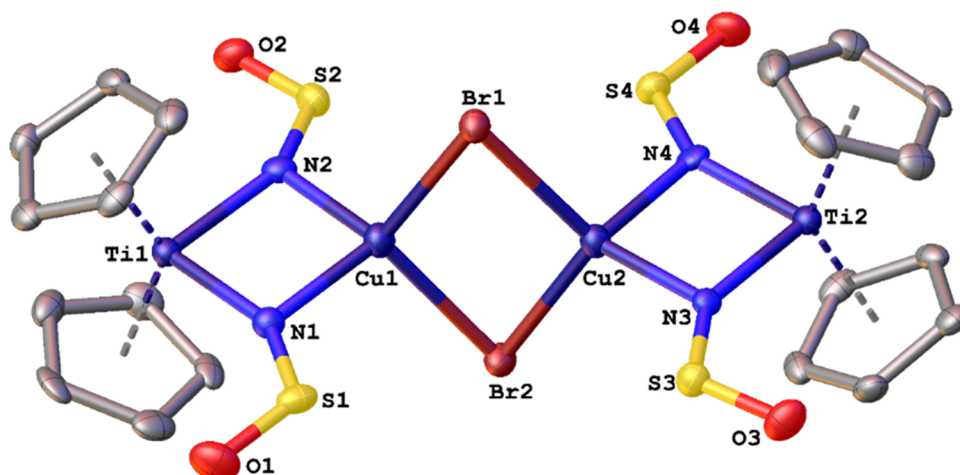
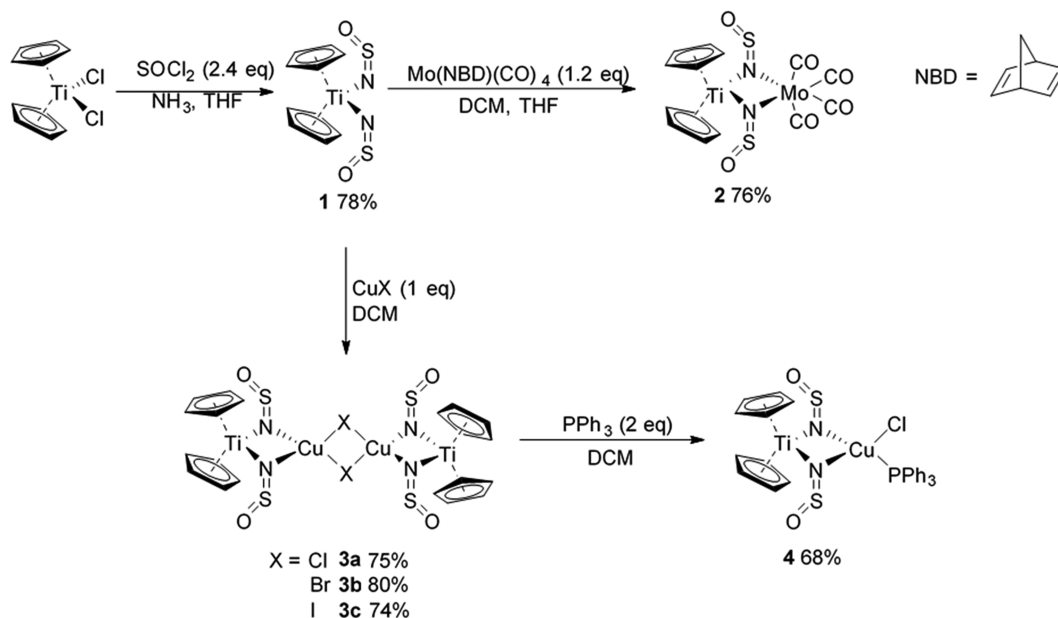


Figure 2. Thermal ellipsoid plot (50% probability ellipsoids) of **3b**. Hydrogen atoms and solvent molecules omitted for clarity.

114.6 ppm for **1**), 204.7, and 217.2 ppm. The IR spectrum also showed only minor changes, including the expected introduction of signals associated with the CO ligands. However, the ^{14}N NMR spectrum of **2** shows a rather dramatic downfield shift from 82.5¹⁷ to 400 ppm relative to nitromethane for **1** and **2**.

We expanded on the synthesis of bimetallic species by the reaction of **1** with CuX ($\text{X} = \text{Cl}, \text{Br}, \text{and I}$) to give tetrametallic dimers of the type $[\text{Cp}_2\text{Ti}(\text{NSO})_2\text{CuX}]_2$ (Scheme 1). **3a–3c** were obtained in good yields and gave satisfactory elemental analyses. **3a** was further reacted with triphenylphosphine to give **4**. While this reactivity was not confirmed for **3b** and **3c**, we see no reason to expect they would not produce analogous results. **4** was also synthesized directly by the reaction of **1** with CuCl in the presence of triphenylphosphine. The ^1H and ^{13}C NMR spectra of compounds **3a–3c** and **4** show even less differentiation from **1** than **2**, with virtually identical spectra (see the Supporting Information, SI).

Crystals of **3a–3c** suitable for single-crystal X-ray diffraction were grown by cooling saturated chloroform solutions (Table 1 and Figure 2). The structures of **3a–3c** consist of central Cu_2X_2 cores with tetrahedral copper centers coordinated by the halides and two nitrogen atoms from the thionylimido ligand. The Cu_2X_2 geometry is influenced by the nature of the halogen in a fashion similar to that of previous examples,¹⁸ with the $\text{Cu}\cdots\text{Cu}$ distance being significantly shorter for the iodine case. The thionylimido ligand geometry resembles that in **2**, with a similar contraction on the N–S–O angles relative to that of mononuclear complexes. There are chloroform solvate molecules in the structures of **3a** and **3b**, which may be responsible for the axial torsion in one of the independent molecules in **3a** (Figure S1). The structure of **4** (Figure 3) has features similar to those of **3a–3c**.

As examples, **2** and **3c** were investigated computationally and the Wiberg bond indices (WBIs) computed between titanium and the nearest metal atom in the complexes as 0.30 and 0.27, respectively (RI-BP86 level; see the SI for details)

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3a (Two Independent Molecules), 3b, 3c, and 4

	3a	3a	3b	3c	4
Ti1–N1	2.049(7)	2.032(7)	2.042(4)	2.040(12)	2.0330(18)
Ti1–N2	2.017(7)	2.045(8)	2.057(4)	2.039(12)	2.0479(18)
Ti2–N3		2.042(7)	2.060(4)		
Ti2–N4		2.040(7)	2.043(4)		
Cu1–N1	1.984(7)	1.999(7)	2.040(3)	2.067(12)	2.0898(17)
Cu1–N2	2.046(7)	1.999(8)	2.024(4)	2.064(11)	2.0833(18)
Cu2–N3		2.006(7)	2.003(3)		
Cu2–N4		2.003(7)	2.052(4)		
Cu1–X1	2.324(3)	2.310(3)	2.4791(8)	2.598(2)	2.2905(7)
Cu1–X2/P1	2.365(3)	2.330(3)	2.4679(7)	2.625(2)	2.2222(7)
Cu2–X1		2.355(3)	2.4756(8)		
Cu2–X2		2.308(3)	2.4709(7)		
N1–S1	1.501(7)	1.500(7)	1.503(4)	1.480(13)	1.4953(18)
N2–S2	1.487(7)	1.497(8)	1.512(4)	1.487(13)	1.4944(18)
N3–S3		1.495(7)	1.515(4)		
N4–S4		1.458(7)	1.505(4)		
S1–O1	1.473(7)	1.454(7)	1.470(3)	1.456(13)	1.4555(18)
S2–O2	1.443(8)	1.461(8)	1.466(3)	1.432(12)	1.4542(18)
S3–O3		1.459(7)	1.460(3)		
S4–O4		1.458(7)	1.474(3)		
N1–S1–O1	116.6(4)	117.1(4)	117.7(2)	116.9(7)	117.69(11)
N2–S2–O2	117.3(4)	117.2(5)	117.38(19)	117.1(7)	117.43(11)
N3–S3–O3		117.4(4)	117.11(19)		
N4–S4–O4		116.8(4)	117.77(19)		
N1–Ti1–N2	93.0(3)	93.9(3)	92.38(14)	92.5(5)	91.05(7)
N3–Ti2–N4		93.5(3)			
N1–Cu1–N2	94.1(3)	96.3(3)	93.42(14)	91.0(5)	88.50(7)
N3–Cu2–N4		95.8(3)	94.28(14)		
Ti1–N1–Cu1	86.8(3)	85.1(3)	87.10(14)	88.1(5)	90.31(7)
Ti1–N2–Cu1	86.0(3)	84.7(3)	87.10(14)	88.3(5)	90.09(7)
Ti2–N3–Cu2		85.3(3)	86.86(14)		
Ti2–N4–Cu2		85.4(3)	86.01(14)		
Cu1–X1–Cu2	75.38(8)	76.07(8)	70.71(2)	60.98(8)	
Cu1–X2–Cu2		76.61(8)	70.72(2)		
Ti1...Cu1	2.7708(19)	2.726(2)	2.8120(10)	2.857(3)	2.9235(5)
Ti2...Cu2		2.7420(19)	2.7931(10)		
Cu1...Cu2	2.867(2)	2.8747(16)	2.8627(8)	2.650(4)	
X1...X2	3.711(4)	3.657(4)	4.033(4)	4.501(4)	
S...S	4.946(4)	5.018(4)	4.494(4)	4.917(4)	
S...S		5.230(4)	5.241(4)		

and indicate significant metal–metal bonding in these complexes as a result of weak d–d overlap (Figure 4), potentially contributing to their stability. While organic compounds tend to have WBIs close to 1, 2, and 3 for formal single, double, and triple bonds, respectively, much smaller WBIs are usually obtained for formal metal–metal bonds. For comparison, WBIs of 0.18 and 0.29 have been reported for dinuclear complexes with formal Fe–Fe and Cr–Cr single bonds, respectively.¹⁹ The M–M bond lengths can also be analyzed by considering the “formal shortness ratio” (FSR), i.e., the ratio of the metal–metal distance to the sum of the single-bond atomic radii of the two metal ions.²⁰ For 3a–3c, this ratio is around 0.94, whereas for 2, the value is ca. 1.02; both values are in accordance with the WBI and suggest significant M–M bonding. For comparison, in a Ti–Cu system supported by phosphoramidate ligands, Wu et al.²¹ found a Cu–Ti distance of 2.9419(5) Å.

The electrochemistry of complexes 1–3 was investigated by cyclic voltammetry (CV; see the SI). 1 shows a quasi-irreversible reduction at –1.424 V. The copper complexes all show irreversible processes for both reduction and oxidation. The irreversible behavior of the copper complexes upon reduction in CV may be due to the loss of a halide ion. In contrast, 2 has a fully reversible first reduction, with an irreversible second reduction and two irreversible oxidations (Figure 5). This change of the first reduction from quasi-irreversible in 1 to fully reversible in 2 is likely due to the stabilizing effect of incorporation into the ring, making ligand dissociation less favorable.

In summary, we have reported the first examples of the thionylimido ligand acting as a μ_2 bridge between two transition-metal atoms. These were synthesized by the use of a titanocene scaffold as a supporting structure; the metal–metal bonding in these systems is significant and likely to

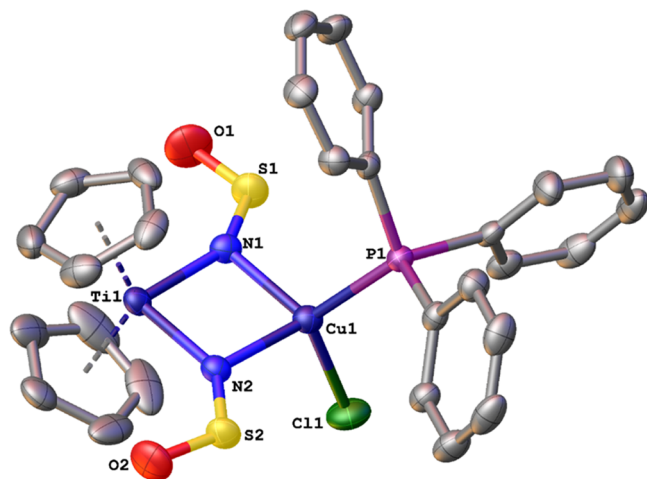


Figure 3. Thermal ellipsoid plot (50% probability ellipsoids) of **4**. Hydrogen atoms omitted for clarity.

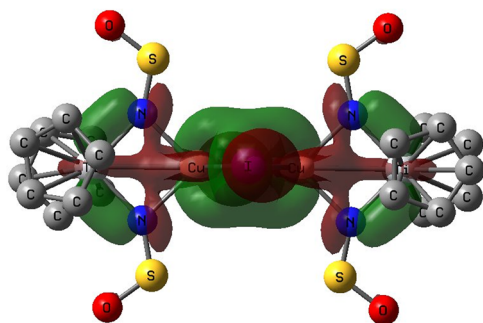


Figure 4. "Top view" of molecular orbital 164 for **3c** along the I...I axis, showing the weak overlap between in-phase d orbitals on the metals, facilitated by overlap with lone-pair orbitals on nitrogen and iodine (isodensity value for plotting 0.02 au; hydrogen atoms omitted for clarity).

contribute to their stability. All complexes were synthesized in good-to-excellent yields and characterized by multinuclear NMR, IR, and single-crystal X-ray crystallography.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00725>.

Full experimental details and methods, computational methods, additional crystallographic information, additional figures, and electrochemical data (PDF)

Accession Codes

CCDC 1985296–1985300 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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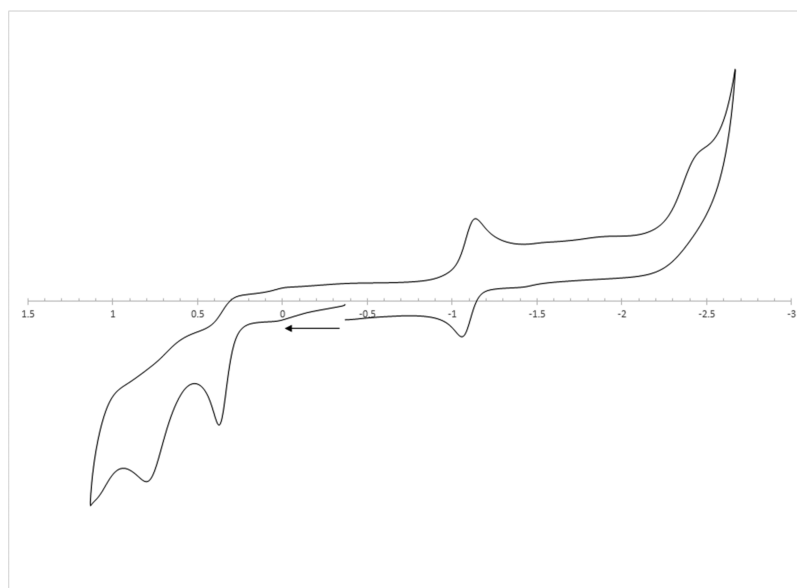


Figure 5. Cyclic voltammogram of **2** from 1.2 to -2.5 V (vs Fc/Fc⁺) at a scan rate of 0.1 V s⁻¹ showing two reduction and three oxidation processes.

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Author Contributions

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Notes

The authors declare no competing financial interest. Underpinning data is available at the University of St Andrews Research Portal: <https://doi.org/10.17630/Obf163c5-ad55-4e38-a245-e15c5630eb16>.

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