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 to 89.24(9)° in 2 and the increase of the Ti−N distance from 2.013(2) Å in 1 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 Pt(PMe3)2(NSO)2 [123.3(8) and 121.4(8)°].

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), while 13C NMR showed the three expected resonances at 115.8 (cf. 116.49(13)), 116.82(13), and 116.49(13) ppm, respectively.

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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 82.5 to 400 ppm relative to nitromethane for 1.

We expanded on the synthesis of bimetallic species by the reaction of 1 with CuX (X = Cl, Br, and I) to give tetrametallic dimers of the type [Cp$_2$Ti(NSO)$_2$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 $^1$H 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$_2$X$_2$ cores with tetrahedral copper centers coordinated by the halides and two nitrogen atoms from the thionylimido ligand. The Cu$_2$X$_2$ geometry is influenced by the nature of the halogen in a fashion similar to that of previous examples, with the Cu···Cu distance being significantly shorter for the iodine case. The thionylimido ligand geometry resembles that in 2, with 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).
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. 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. 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. 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 μ1 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
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

* 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 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).

Figure 5. Cyclic voltamogram 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.
AUTHOR CONTRIBUTIONS

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Notes

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