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COMMUNICATION

Synthesis, molecular and electronic structure, and reactions of a Zn–Hg–Zn bonded complex

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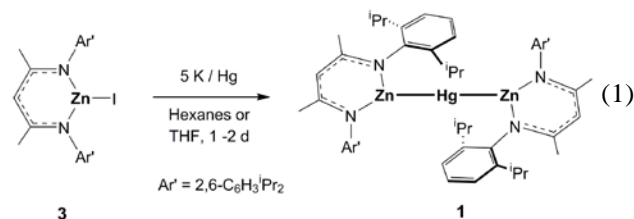
Reaction of (^{Ar'}NacNac)ZnI with potassium/mercury amalgam gave the trimetallic compound {(^{Ar'}NacNac)Zn}₂Hg (1**) containing a Zn–Hg–Zn unit and the first example of a bond between two different Group 12 metals; DFT and QTAIM analyses suggest that **1** is best described as two formally Zn(I) atoms with a Hg(0) atom positioned between them; reactions of **1** with stoichiometric I₂, FpI or Fp₂ gave addition products of the type (^{Ar'}NacNac)ZnX (X = I, Fp) and Hg. ^{Ar'}NacNac = HC{C(Me)N(2,6-C₆H₃ⁱPr₂)₂}; Fp = CpFe(CO)₂.**

Development of the synthesis, properties and reactions of molecular compounds containing unusual metal-metal bonds is a field of considerable continuing interest.¹ Of particular relevance to our present contribution are bonds between pairs of the Group 12 elements, Zn,² Cd,³ and Hg. Overviews of this area have recently been published.⁴

Compounds of the type M₂X₂ (X = a formally monoanionic ligand) contain metals in the formal +1 oxidation state.⁵ While mercury(I) monohalides Hg₂X₂ (X = halogen)⁶ have been known since at least the 19th century, their Group 14 analogues (X = aryl, silyl) were reported only recently.^{3b, 7} The chemistry of the molecular Cd^I and Zn^I counterparts of Hg₂X₂ is, by contrast, very much in its infancy. In 2004 Carmona *et al.* reported the first Zn(I) compound, Cp*₂Zn₂ obtained initially from the reaction of Cp*₂Zn with Et₂Zn.^{2a, 2b} A number of other low valent Zn–Zn bonded molecules has since been described,^{4b} typically involving chelating supporting ligands such as ^RNacNac (^RNacNac = HC{C(Me)NR}₂).^{2c-g} Also recently, following Reger's earlier report of (Tp^{Me2})₂Cd₂ (Tp^{Me2} = HB(3,5-N₂C₃HMe₂)₃), Power reported the synthesis and structural characterisation of Ar*₂Cd₂ (Ar* = 2,6-C₆H₃Ar', Ar' = 2,6-C₆H₃ⁱPr₂) and its Zn–Zn and Hg–Hg counterparts. Together, these form the first homologous, molecular M^I–M^I bonded series for the Group 12 metals.

In addition to bimetallics of the type Hg₂X₂, mercury readily forms catenated derivatives containing Hg–Hg–Hg (or longer) linkages.^{6, 8} By far the most common of these are the formally mixed-valence (Hg^{II}₂Hg⁰) *triangulo* species⁹ containing a Lewis base-stabilised, two-electron [Hg₃]⁴⁺ unit (e.g. Hg₃{μ₂-(Ph₂P)₂N}₄).^{8, 10} Only one structurally authenticated example of a compound containing a linear Hg–Hg–Hg moiety has been described, namely Cp₂Nb{Hg(S₂NCEt₂)₃}.¹¹ Such homocatenated [M_n]^{m+} species are

unknown for Cd and Zn, but, like Hg itself, both form M'–M–M' heterobimetallic linkages with M' being a transition metal or post-transition-metal from outside Group 12.^{8, 12} An exception to this general motif is Fischer's mixed valence (with respect to Zn) compounds containing Cp*₂Zn^I–Zn⁰–TM (TM = transition metal) linkages, formed from Cp*₂Zn₂ and certain low oxidation state TM precursors.¹³ These authors also described a number of other interesting reactions of Cp*₂Zn₂ with d¹⁰ complexes forming products such as Cp*M(ZnCp*)₃ (M = Ni, Pt) containing Cp*Zn moieties as one-electron donor ligands.¹² Here we report the synthesis, electronic and molecular structure and preliminary reactivity of {(^{Ar'}NacNac)Zn}₂Hg (**1**).



One widely-applicable synthetic route to new metal-metal bonded compounds is the reduction of a higher oxidation state halide precursor.¹ This approach has been used to prepare a number of Zn–Zn compounds,^{4b} including Robinson's (^{Ar'}NacNac)₂Zn₂ (**2**), made by potassium metal reduction of (^{Ar'}NacNac)Zn(μ-I)₂Li(OEt₂)₂ in toluene.^{2c} In the course of our studies of compounds with new metal-metal bonds¹⁴ we carried out the reduction of (^{Ar'}NacNac)ZnI (**3**) with potassium-mercury amalgam, also in toluene. Under these conditions, only trace amounts of (^{Ar'}NacNac)₂Zn₂ were formed as judged by ¹H NMR analysis of the crude reaction mixture, and instead a new compound {(^{Ar'}NacNac)Zn}₂Hg (**1**) was the major product. Repeating the reaction in hexanes or THF using potassium/mercury amalgam (2% w/w) gave **1** in *ca.* 80% isolated yield as orange crystals after one or two days at room temperature (Eq. 1, Fig. 1).[†]

Molecules of **1** have approximate C_{2h} molecular symmetry. A central Hg(1) atom is coordinated in a linear manner (Zn–Hg–Zn = 180 ° to two distorted (^{Ar'}NacNac)Zn moieties with significantly different Hg(1)–Zn(1)–N(1,2) angles of 153.37(6)

and 111.85(6)° and Zn(1)-N(1,2) distances of 1.9643(19) and 2.002(2) Å. Compound **1** is the first reported Zn–Hg bond and the first example of any bond between two different Group 12 elements, and also the first example of *heterocatenation* of Group 12 elements. The Zn(1)–Hg(1) distance of 2.4846(3) has no direct structural precedent, but can be compared with the sum of the covalent radii compiled by Alvarez (2.54 Å) and Pyykkö (2.51 Å),¹⁵ and the value estimated (2.466 Å) by additive extrapolation from Robinson's (^{Ar'}NacNac)₂Zn₂ (three-coordinate Zn–Zn = 2.3586(7) Å^{2c}) and Power's Ar*₂Hg₂ (two-coordinate Hg–Hg = 2.5738(3) Å^{3b}). Mechanistically, compound **1** probably forms *via* formation of a transient (^{Ar'}NacNac)Zn radical intermediate which is intercepted by the excess of Hg (*ca* 500 molar equivs) at the solution/Hg interface at a faster rate than by another transient Zn(I) radical, as is well-precedented in amalgam reduction chemistry.¹⁶

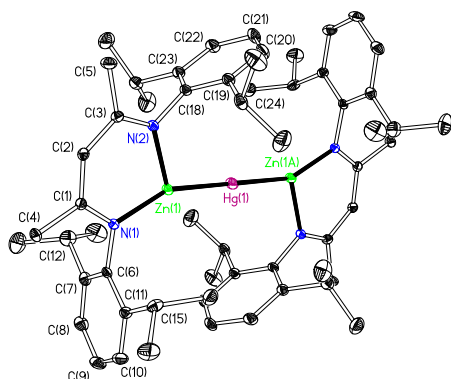


Figure 1. Displacement ellipsoid plot (20%) of $\{(\text{Ar}'\text{NacNac})\text{Zn}\}_2\text{Hg}$ (**1**). H atoms omitted. Selected distances (Å) and angles (°) with average DFT values for **1** in brackets: Zn(1)–Hg(1) 2.4846(3) [2.515], Zn(1)–N(1) 1.9643(19) [1.980], Zn(1)–N(2) 2.002(2) [2.038], Zn(1)–Hg(1)–Zn(1A) 180.0 [180.0], N(1)–Zn(1)–Hg(1) 153.37(6) [158.7], N(2)–Zn(1)–Hg(1) 111.85(6) [107.2]. Atom with the suffix 'A' are related to their counterparts by the symmetry operator 1-x, 1-y, 1-z.

Relativistic DFT calculations (Gaussian 09 Rev D.01†) at the PBPBE level incorporating dispersion corrections,¹⁷ in conjunction with Quantum Theory of Atoms in Molecules (QTAIM) analyses¹⁸ have been used to gain an understanding of the molecular and electronic structure of **1**. A number of model compounds and molecular fragments were used to assist with the analyses (see Fig. 2 and the ESI†). DFT reproduced the structure of $\{(\text{Ar}'\text{NacNac})\text{Zn}\}_2\text{Hg}$, and in particular the tendency of the geometry at Zn towards T-shaped and away from the ubiquitous trigonal planar one with approximately equivalent N–Zn–X angles found for three-coordinate (^RNacNac)ZnX and related compounds.⁸ For example, the X-ray structure of (^{Ar'}NacNac)ZnI (**3**)† has N–Zn–I angles of 124.48(11) and 134.45(11)° (av. 129.5°); the N–Zn–Zn angles in **2** (av. *ca.* 132.5 ± 1.5°) span an even narrower range but with an average value close to that in **1** for N–Zn–Hg (132.6°).

The distorted geometry at Zn for **1** is attributable to additional interactions between the Ar' groups of N(2, 2A) and Hg(1). Such interactions around the equatorial belt of otherwise two-coordinate Hg atoms are well-known.^{6, 8} Although the closest Hg(1)⋯C(Ar' ring) contacts (3.589(1), 3.653(1) Å) are long compared to crystallographically determined, unconstrained intermolecular Hg⋯arene contacts (range *ca.* 2.35 – 2.75 Å),⁸ they are comparable to the sum of the van der Waals radii (*ca.*

3.4 – 4.2 Å) for C and Hg.^{19,20} The hypothetical radical fragment (^{Ar'}NacNac)ZnHg (**I**, Fig. 2) also has a distorted geometry at Zn and inequivalent Hg–Zn–N angles (111.8 and 152.6°), thus ruling out intramolecular van der Waals interactions between neighboring ^{Ar'}NacNac groups on Zn(1) and Zn(1A) as the origin of the distortion. The model compound $\{(\text{H}^{\text{NacNac}}\text{Zn})_2\text{Hg}$ (**II**, Fig. 2) with H in place of Ar' exhibits no significant distortion at Zn, confirming the role of the intramolecular Hg⋯arene contacts. Additional calculations on (^{Ar'}NacNac)Zn₂Hg with the four N–Zn–Hg angles constrained to the average value for **1** (132.9°) gave the DFT structure **1-fixed** that was only 3.6 kJ mol⁻¹ less stable than **1**, with a slightly shorter Zn–Hg bond length (2.495 Å) and equivalent Zn–N distances (1.994 Å). Consistent with this, only one Ar' environment was found by NMR spectroscopy at -80 °C. To estimate the cost in energy of distorting the geometry at Zn from trigonal planar we constrained the N–Zn–Hg angles of $\{(\text{H}^{\text{NacNac}}\text{Zn})_2\text{Hg}$ to those in **1** while allowing the rest of the structure to optimise. This gave a destabilisation of 15.6 kJ mol⁻¹, a negligible change in the Zn–Hg distance (2.567 vs. 2.563 Å) but different Zn–N distances (1.959 and 2.019 Å) as found in **1**. Thus the two pairs of Hg⋯Ar' interactions in **1** appear to be worth *ca.* 20 kJ mol⁻¹.

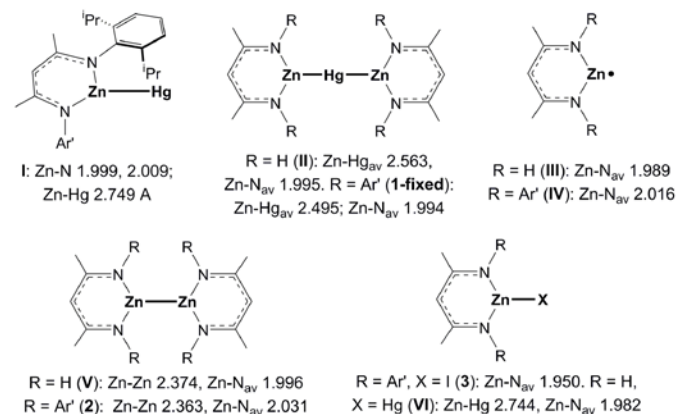


Figure 2. Model compounds studied by DFT, with selected bond parameters (Å).

Analysis of the DFT MOs of **1**, **1-fixed** and **II** found similar bonding situations, supported by the QTAIM analysis of the electron density and charges summarised in entries 1-3 of Table 1. Figure 3 shows the two occupied valence MOs in **II** of predominantly metal character, HOMO and HOMO-7. The HOMO (Fig. 3(a)) has mainly Zn character (56% 4s and 24% 4p) and just 7% Hg (6p) character. From a fragment orbital point of view this represents a bonding interaction of the Hg 6p AO oriented along the Zn–Hg–Zn vector with the out-of-phase linear combination of the two α -SHOMOs of (^HNacNac)Zn (**III**, see the ESI) which have a computed energy of -3.50 eV. The energy of the HOMO in **1** (-3.65 eV) is thus only slightly lower than that of the principal contributing fragment MOs, indicative of a relatively weak interaction. In comparison, the HOMO of the Zn–Zn bonded model compound (^HNacNac)₂Zn₂ (**V** in Fig. 2; 78% Zn character, in agreement with previous reports^{2c}) lies at -4.44 eV (-0.96 eV more stable than the α -SHOMOs of **III**). HOMO-7 (Fig. 3(b)) has mainly Hg 6s character (69%) and only 12% Zn character. It represents the in-phase combination of two α -SHOMOs with the 6s AO of Hg, and lies at -6.92 eV because of substantial relativistic

stabilisation. The computed energy of the 6s AO of Hg in our studies is -6.79 eV and thus HOMO-7 is also not substantially stabilised relative to its predominantly contributing orbital.

Table 1. Selected QTAIM data (atomic units). Values for ρ (electron density), $\nabla^2\rho$ (electron density Laplacian), H (energy density) were obtained at the bond critical point. $\delta(A-B)$ is the delocalisation index for the stated pair of atoms.

Entry	Compound	A, B pair	ρ	$\nabla^2\rho$	H	$\delta(A-B)$	$Q(A)$	$Q(B)$
1	$\{(\text{Ar}^i\text{NacNac})\text{Zn}\}_2\text{Hg}$ (1)	Zn, Hg	0.065	0.069	-0.020	0.763	0.665	-0.139
2	$\{(\text{Ar}^i\text{NacNac})\text{Zn}\}_2\text{Hg}$ (1-fixed)	Zn, Hg	0.067	0.067	-0.021	0.792	0.678	-0.165
3	$\{(\text{H}^i\text{NacNac})\text{Zn}\}_2\text{Hg}$ (II)	Zn, Hg	0.060	0.060	-0.017	0.859	0.644	-0.216
4	$(\text{Ar}^i\text{NacNac})_2\text{Zn}_2$ (2)	Zn, Zn	0.063	0.033	-0.023	0.818	0.594	0.593
5	$(\text{H}^i\text{NacNac})_2\text{Zn}_2$ (V)	Zn, Zn	0.062	0.032	-0.022	0.937	0.545	0.546
6	$(\text{Ar}^i\text{NacNac})\text{Zn}$ (IV)	Zn, none	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	0.585	<i>n.a.</i>
7	$(\text{Ar}^i\text{NacNac})\text{ZnI}$ (3)	Zn, I	0.069	0.085	-0.024	0.888	0.934	-0.428

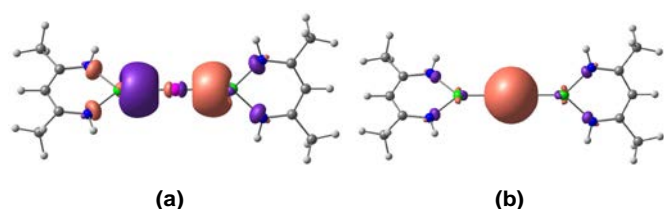


Figure 3 Principal metal-based MOs and their isosurfaces (0.06 au) and energies (eV) for $(\text{H}^i\text{NacNac})\text{Zn}_2\text{Hg}$ (**II**) (a) -3.65 (HOMO), (b) -6.92 (HOMO-7). Zn, Hg, C and N atoms are shown in green, magenta, grey and blue, respectively

QTAIM analysis supports the existence of Zn-Hg bonds in finding bond paths, and selected data for **1** and a number of other species at the respective bond critical points (BCPs) are given in Table 1. The small positive values of both ρ and its Laplacian $\nabla^2\rho$ and the small negative value for H (energy density) for **1**, **1-fixed** and **II** (entries 1-3) are very characteristic of homo- and hetero-nuclear metal-metal bonded compounds in general,^{14a, 21} and in fact comparable to the values for both full (**2**) and 'small' (**V**) models of $(\text{Ar}^i\text{NacNac})_2\text{Zn}_2$ (entries 4 and 5). Table 1 also lists delocalisation indices ($\delta(A-B)$) between the respective pairs of atoms. ($\delta(A-B)$ is a measure of the number of electron pairs delocalised or shared between pairs of atoms and can relate to formal bond order). The values for $\delta(\text{Zn-Hg})$ are indicative of formal single bonds, although systematically slightly smaller than $\delta(\text{Zn-Zn})$ for the same $^i\text{NacNac}$ ligand (*cf* entries 2 *vs.* 4, 3 *vs.* 5), consistent with the more localised bonding implied by the Mulliken analyses of the MOs in **II**. Concerning **1** *vs.* **1-fixed** is it apparent that restricting the intramolecular Hg...arene interaction in the latter case (with the aforementioned shortening of Zn-Hg distances by *ca.* 0.02 Å) gives no significant effect other than that expected from the slightly shorter Zn-Hg bonds.

We have also computed the bond dissociation enthalpies (BDE) for several of the systems of interest. The BDEs for **V** and **2** (i.e. for the process $(^i\text{NacNac})_2\text{Zn}_2 \rightarrow 2(^i\text{NacNac})\text{Zn}$ in its relaxed geometry) were 278.4 and 339.6 kJ mol⁻¹, the former of which compares well with values reported previously for Cp^*Zn_2 and a different model of **2**, $\{\text{HC}\{\text{CHN}(\text{H})\}_2\text{Zn}_2$ (*ca.* 270 – 284 kJ mol⁻¹). The larger value for **2** is because we have

included corrections for dispersion (van der Waals) interactions which were not included in the previous calculations.

The overall $\Delta_r H$ for $\{(\text{H}^i\text{NacNac})\text{Zn}\}_2\text{Hg} \rightarrow 2(\text{H}^i\text{NacNac})\text{Zn} + \text{Hg}$ was 250.3 kJ mol⁻¹, and 340.3 kJ mol⁻¹ for $\{(\text{Ar}^i\text{NacNac})\text{Zn}\}_2\text{Hg} \rightarrow 2(\text{Ar}^i\text{NacNac})\text{Zn} + \text{Hg}$, giving *average* Zn-Hg BDEs of *ca.* 125.1 and 170.2 kJ mol⁻¹. These are only about half of the analogous Zn-Zn BDEs, but the average values do not tell the whole story. Calculation of the stepwise BDEs for $(^i\text{NacNac})\text{Zn}_2\text{Hg} \rightarrow (^i\text{NacNac})\text{ZnHg} + (^i\text{NacNac})\text{Zn}$ and then $(^i\text{NacNac})\text{ZnHg} \rightarrow (^i\text{NacNac})\text{Zn} + \text{Hg}$ gave values of 214.1 and 36.2 (R = H) and 286.8 and 53.6 (R = Arⁱ) kJ mol⁻¹, respectively, showing that cleavage of the first Zn-Hg bond is much more endothermic than the second. The difference between the two second BDE values (36.2 *vs.* 53.6 kJ mol⁻¹) mainly reflects the intramolecular Hg...arene interaction which is present in $(\text{Ar}^i\text{NacNac})\text{ZnHg}$ (**I**, Fig. 2) but not in $(\text{H}^i\text{NacNac})\text{ZnHg}$.

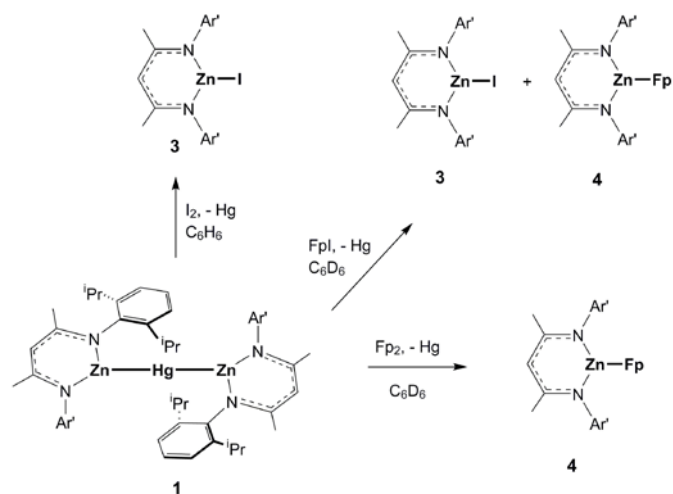
Interestingly, $\Delta_r H$ for the Hg elimination reaction $(^i\text{NacNac})\text{Zn}_2\text{Hg} \rightarrow (^i\text{NacNac})_2\text{Zn}_2 + \text{Hg}$ was only 0.8 kJ mol⁻¹ for R = Arⁱ and -28.1 kJ mol⁻¹ for R = H. This implies that Zn-Zn bond formation from **1** should be thermodynamically favourable but that kinetic factors restrict this process. Experimentally, heating solutions of **1** at 70 °C for 16 hours gave no reaction, consistent with this interpretation. Photolysis (Hg vapour lamp) at room temperature for 18 hours gave slow decomposition to unknown products.

The MO description of the Zn-Hg-Zn bond in **1** as having a HOMO with mainly Zn character and HOMO-7 that is mainly Hg character is supported by the QTAIM atomic charges $Q(\text{Zn})$ and $Q(\text{Hg})$. Thus for the Zn(I) radical $(\text{Ar}^i\text{NacNac})\text{Zn}$ (**IV**) $Q(\text{Zn})$ changes little (+0.585 to +0.594) upon forming $(\text{Ar}^i\text{NacNac})_2\text{Zn}_2$ (**2**, also formally ZnI), whereas $Q(\text{Zn})$ for the Zn(II) iodide $(\text{Ar}^i\text{NacNac})\text{ZnI}$ (**3**) increases to 0.934 upon formal oxidation of the Zn(I) centre, with 0.428 electrons being transferred overall to iodide ($Q(\text{I}) = -0.428$). In contrast, $Q(\text{Zn})$ increases by only 0.08 from **IV** to **1**, with $Q(\text{Hg})$ showing that less than 0.07 electrons are transferred per $(\text{Ar}^i\text{NacNac})\text{Zn}$ fragment upon coordinating to Hg in **1**. This increase in formal charge in the case of **3**, but not for **1** or **2**, is reflected in the much shorter computed Zn-N_{av} bond distances for **3** (1.950 Å) than in **1** (2.009), **1-fixed** (1.994 Å), **2** (2.031 Å) or **IV** (2.016 Å). These are supported by experiment for **3** (Zn-N_{av} = 1.922(4) Å), **1** (Zn-N_{av} = 1.984(3) Å) and **2** (Zn-N_{av} = 2.009(4) Å). Overall, **1** is best described

as a $[\text{Zn}(\text{I})_2\text{Hg}(0)]$ system with only a small degree of charge transfer from Zn(I) to Hg(0) upon Zn–Hg bond formation.

Initial studies indicate that compound **1** does indeed react as if it were a source of Zn(I) (Scheme 1). Reaction with I_2 (1 equiv.) on both the NMR-tube scale and on scale-up gave quantitative conversion to $(^{\text{Ar}}\text{NacNac})\text{ZnI}$ (**3**) and elemental mercury.

In a similar way, reaction of **1** with FpI (Fp = $\text{CpFe}(\text{CO})_2$) in C_6D_6 quantitatively formed **3** and $(^{\text{Ar}}\text{NacNac})\text{ZnFp}$ (**4**).[†] Compounds **3** and **4** could not be separated on a preparative scale due to their similar solubilities, but **4** was prepared independently from **3** and KFP and crystallographically characterised (see the ESI). Reaction of **1** with 2 equiv. FpI gave almost exclusively **3** and the known²² HgFp_2 . DFT calculations appear to be consistent with the thermodynamic reaction outcome and found $\Delta_r H = -161.0 \text{ kJ mol}^{-1}$ for $\{(^{\text{Ar}}\text{NacNac})\text{Zn}\}_2\text{Hg} + 2 \text{ FpI} \rightarrow 2 (^{\text{Ar}}\text{NacNac})\text{ZnI} + \text{HgFp}_2$ but only $-84.5 \text{ kJ mol}^{-1}$ for the alternative outcome, $\{(^{\text{Ar}}\text{NacNac})\text{Zn}\}_2\text{Hg} + 2 \text{ FpI} \rightarrow 2 (^{\text{Ar}}\text{NacNac})\text{ZnFp} + \text{HgI}_2$ (NB these are gas phase values and do not take into account solvation, lattice energy, or entropy effects). Finally, **1** also reacted with Fp_2 (either 0.5 or 1 equiv.) in C_6D_6 . Interestingly, regardless of stoichiometry, only 0.5 equiv. of the Fp_2 was consumed to give ca. 50% conversion of **1** to $(^{\text{Ar}}\text{NacNac})\text{ZnFp}$ (**4**) with the rest of the **1** being converted to an unknown mixture of several other compounds appearing to contain a $^{\text{Ar}}\text{NacNac}$ moiety according to ^1H NMR spectroscopy.



Scheme 1. Reactions of $\{(^{\text{Ar}}\text{NacNac})\text{Zn}\}_2\text{Hg}$ (**1**).

In summary, we have reported the synthesis and bonding of a unique heterocatenate of the Group 12 metals containing Zn(I)-like metal centres, as also revealed by initial reactivity studies. Work is underway in our laboratories to develop further the chemistry of **1** and its intermetallic homologues.

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Notes and references

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[†] Electronic Supplementary Information (ESI) available: characterising data, crystallographic data in CIF format (CCDC 1044305-1044307), and further computational details. See DOI: 10.1039/c000000x/

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Graphical abstract

