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Synthesis of d^{10} *N*-Heterocyclic Carbene Complexes with a Perimidine Scaffold

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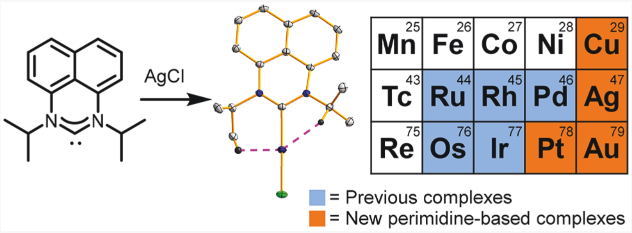
ABSTRACT: *N*-Heterocyclic carbenes (NHCs) are vital auxiliary ligands for organometallic chemistry, and although many variants have been synthesized, by far the most common are based on five-membered rings, such as imidazole or benzimidazole. Unlike NHC complexes built on five-membered rings, which are typically conjugated, exploration of six-membered-ring NHC variants has focused on nonconjugated versions, such as *N*,*N*′-diamidocarbenes. Reports of conjugated six-membered ring NHCs are limited to metal complexes with a perimidine scaffold that are in a narrow range of between six and eight d electrons (on metals from groups 8−10). This manuscript showcases the synthesis of four d^{10} metal complexes with a perimidine scaffold. The gold and silver complexes have a linear geometry, while the copper and platinum complexes are three-coordinated. All complexes were characterized by single-crystal X-ray crystallography, multinuclear NMR, and additional spectroscopic methods.



■ INTRODUCTION

N-Heterocyclic carbenes (NHCs) are critical auxiliary ligands for transition metals, with applications ranging from homogeneous catalysis to surface functionalization.[1−5] While unsaturated examples, such as imidazole- and benzimidazole-based NHCs, dominate the literature (Figure 1A),[6,7] there has been a shift to nonstandard NHCs in recent years that have shown greater effectiveness for catalysis.[8−17] In particular, saturated NHCs (imidazoline-based) have proven a popular choice due to their increased σ-donor strength, despite saturated NHCs being more challenging to synthesize than imidazole variants. Notable examples where saturated NHCs are highly effective include Grubbs second-generation catalyst for olefin metathesis and reactions that induce chirality.[12,18−20]

Remarkably, the case for six-membered-ring NHCs is reversed. The saturated variants have dominated the literature and conjugated examples based on a perimidine scaffold are rare (Figure 1A).[21−27] To date, the complexes that have been characterized are restricted to group 8−10 transition metals with d electron counts of 6 or 8. (Figure 1B). Richeson first reported this class of NHCs and prepared complexes on Rh and Pd.[28−30] Mashima and co-workers later developed iridium complexes for C−H bond activation and catalysis,[31,32] while Hill[33−36] and others[37−39] have developed NHC pincer complexes with a perimidine scaffold for catalytic applications. Finally, a few scattered examples have been synthesized for drug development[40] or fluorescent applications.[41]

In this manuscript, we present the synthesis and characterization of four new perimidine-based NHC metal complexes. All four complexes are d^{10}, and include the first group 11 NHC compounds of this type. All complexes are characterized by

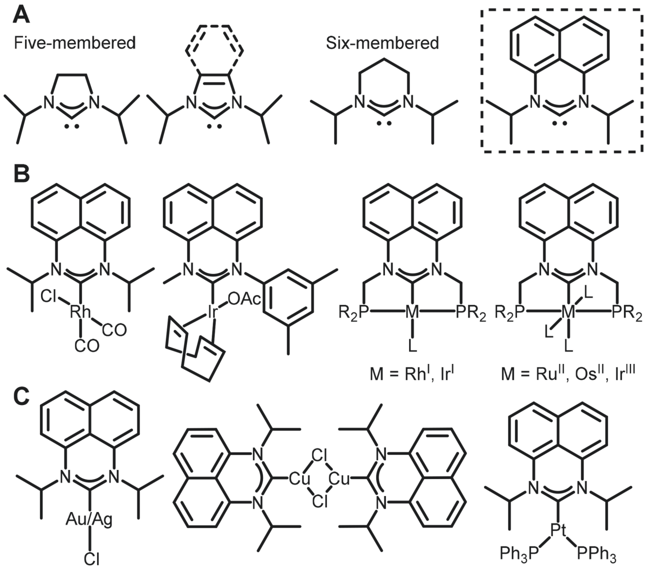


Figure 1. (A) Typical NHCs for five-membered and six-membered rings. (B) Examples of previously reported metal complexes with a perimidine scaffold. All previous examples are on Ru, Rh, Pd (example not shown), Os, and Ir. (C) Newly reported NHC metal complexes in this manuscript.

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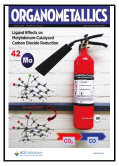

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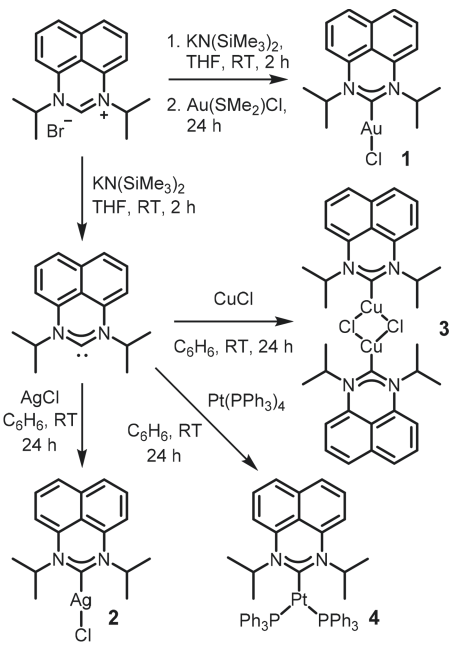
single crystal X-ray diffraction and multinuclear NMR. Finally, we demonstrate that these late transition metal complexes can act as NHC transfer reagents, which will open up this class of NHC across more of the periodic table.

RESULTS AND DISCUSSION

The synthesis of 1,3-diisopropylperimidinium bromide ($(C_{10}H_6(^{i}PrN)_2CH)(Br)$) was originally reported by Richeson[30,42] who also isolated the free carbene 1,3-(^{i}Pr)$_2$-perimidin-2-ylidene, $(C_{10}H_6(^{i}PrN)_2C)$.[29] We employed $(C_{10}H_6(^{i}PrN)_2CH)(Br)$ due to its ease of synthesis from commercial reagents in five steps. The gold complex, $(C_{10}H_6(^{i}PrN)_2C)AuCl$ (**1**), was synthesized through a two-step approach (Scheme 1). In an inert atmosphere, $KN(SiMe_3)_2$ was dissolved in THF and was added to a stirring suspension of the $(C_{10}H_6(^{i}PrN)_2CH)(Br)$ in THF. The reaction mixture was stirred for 2 h, after which it was filtered over a short Celite plug to remove KBr. The solution was added to a vial containing $Au(SMe_2)Cl$, and the reaction was stirred for 1 day. The solvent was removed, and the resulting residue was extracted with methylene chloride and passed over a short Celite plug. The filtrate was then dried and the crude solid was purified through column chromatography to yield **1** as a yellow solid. Notably, pincer-style perimidine-based NHCs do not yield gold complexes since the gold only binds to the phosphine arms; thus, we were excited to prepare the first gold complex with this NHC design.[34,43] Single crystals for X-ray crystallography were grown by layering hexanes over a solution of **1** in methylene chloride.

Scheme 1. Synthesis of NHC Complexes 1−4



For the synthesis of the Pt, Ag, and Cu complexes, we followed one general approach with slight differences for each metal. The free carbene ligand, $(C_{10}H_6(^{i}PrN)_2C)$, was synthesized through deprotonation with $KN(SiMe_3)_2$ in THF, and was isolated and confirmed per Richeson's prior account.[29] The ligand (2 equiv twice for Pt and 1 equiv for the Ag and Cu complexes) was dissolved in benzene and added to the appropriate metal salts, and the reactions were stirred for 24 h (Scheme 1). The platinum complex required excess ligand to drive the reaction to completion since both the NHC and phosphines are similar neutral Lewis bases. The reaction mixtures were filtered over Celite, and the filtrate volume was concentrated to 2 mL. Hexanes were then layered over the concentrated benzene solutions yielding $(C_{10}H_6(^{i}PrN)_2C)AgCl$ (**2**), $[(C_{10}H_6(^{i}PrN)_2C)CuCl]_2$ (**3**), and $(C_{10}H_6(^{i}PrN)_2C)Pt(PPh_3)_2$ (**4**) as yellow single crystals for X-ray crystallography. Unlike **1**, which is stable in air, these complexes are highly sensitive to oxygen and water.

Since so few of these NHC complexes have been structurally characterized, the solid-state structures of these d^{10} complexes are particularly noteworthy. Indeed, all previously published examples, with the exception of a few iridium complexes that are five-coordinate,[32] have given square planar[28−33,35,41,44,45] or octahedral complexes.[31−35,39,46] The solid-state structure for complex **1** shows a two-coordinate linear complex with a Au−C distance of 2.020(3) Å and a C−Au−Cl bond angle of 179.96(8)° (Figure 2A). The Au−C bond distance is slightly longer than isostructural gold complexes with five-membered-ring NHCs[47−49] but shorter than the one example with a saturated six-membered ring.[50] The other notable feature in the crystal structure is the close contacts between the methine protons (which were located in the difference map) and the gold (H12···Au, 2.34 Å, H14···Au, 2.33 Å). These distances are well within the combined van der Waals radii for these atoms, consistent with Richeson's observation that the isopropyl

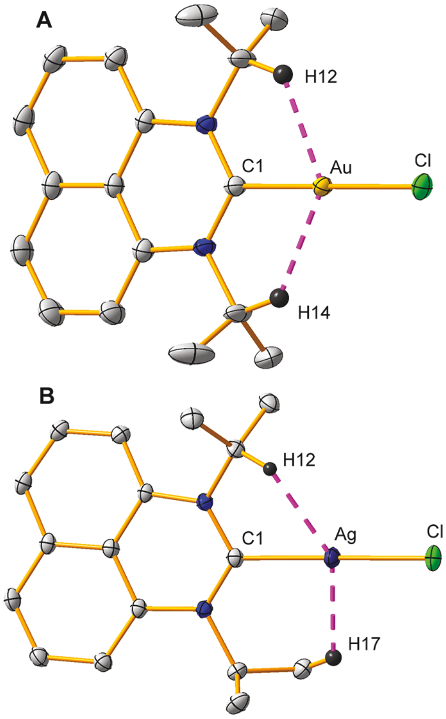


Figure 2. Solid-state structures of (A) $(C_{10}H_6(^{i}PrN)_2C)AuCl$, **1**, and (B) $(C_{10}H_6(^{i}PrN)_2C)AgCl$, **2**. Yellow, indigo, blue, gray, and green ellipsoids (50% probability) represent gold, silver, nitrogen, carbon, and chlorine, respectively. Hydrogen atoms are omitted for clarity unless necessary to display close interatomic interactions (dark gray spheres). Selected bond lengths (Å) and angles (deg): **1** Au−C1, 2.020(3); Au−Cl, 2.3092(8); C1−Au−Cl, 179.96(8); **2** Ag−C1, 2.1312(11); Ag−Cl, 2.3628(3); C1−Ag−Cl, 170.13(3).

groups may not be able to rotate freely for perimidine-based NHCs.[28,29]

The solid-state structure for the silver complex, $(C_{10}H_6({}^{i}PrN)_2C)AgCl$ (**2**) also revealed a two-coordinate geometry at the metal center. In this case, the Ag−C1 bond (2.1312(11) Å) was significantly elongated versus **1**. Notably, direct NHC isostructural analogs (i.e., with isopropyl groups off the nitrogen) with either five- or six-membered rings have not been synthesized on silver. Isopropyl analogs form dimers,[51,52] but switching to more sterically encumbering R-groups can lead to similar two-coordinate complexes.[53−55] However, in both cases the C−Ag bond distances are shorter than **2**. The C1−Ag−Cl angle is also slightly bent at 170.13(3)°. This bend away from linearity may be due to interactions with hydrogen atoms on the NHC ligand. Unlike complex **1**, for **2** the interactions are asymmetric, with one coming from an α-carbon (H12···Ag, 2.43 Å) and the second coming from a β-carbon (H17···Ag, 2.34 Å).

The final group 11 complex that we synthesized, $[(C_{10}H_6({}^{i}PrN)_2C)CuCl]_2$ (**3**) yielded a three-coordinate dimer in the solid-state (Figure 3A) with two bridging chlorides. Complex **3** has the third shortest M−C1 bond distance of any reported perimidine-based NHC complex at 1.932(3) Å.[33,41] The bridging chloride ligands are highly asymmetric with bond distances of Cu−Cl = 2.263(1) Å and Cu−Cl′ = 2.391(1) Å, and there are a few reported examples of similar copper(I) NHC complexes with bridging chlorides.[56,57] Like **1** and **2**, copper complex **3** has a close contact with a methine proton (H12···Cu, 2.20 Å), but in this case, there is only one contact. The asymmetry of the isopropyl groups in the crystal structure stimulated our investigation of **3** in solution via NMR (*vide supra*).

Our final d^{10} complex, $(C_{10}H_6({}^{i}PrN)_2C)Pt(PPh_3)_2$ (**4**) has a trigonal planar geometry in the solid state. The Pt−C1 bond distance is 2.057(3) Å which is in between the distances for **1** and **2**. NHC complexes with Pt(0) are quite rare, and a few three-coordinate species have been reported.[58,59] Most Pt(0) complexes are two coordinate.[60−65] All of these Pt(0) complexes display Pt−C bond distances shorter than those of **4**, and notably all feature five-atom ringed NHCs. The three ligands on **4** form a plane where the Pt is in the center, but the steric bulk from the isopropyl groups on the NHC push the phosphines close together, which reduces the P1−Pt−P2 bond angle to 113.92(3)°. Like the group 11 complexes discussed earlier, complex **4** has close contacts between the metal center and the methine protons (H12···Pt, 2.39 Å; H15···Pt, 2.31 Å).

Since the solid-state structures demonstrated that there are close contacts between the protons on the isopropyl of the NHCs and the metal, we were particularly interested in the ^{1}H NMR spectra. Evaluation of the ^{1}H NMR for $(C_{10}H_6({}^{i}PrN)_2C)AuCl$ shows the influence of the metal center (Figure 4A). In particular, the methine protons are shifted downfield (6.17 ppm) and broadened significantly to where the expected splitting is not observed. In fact, the methine

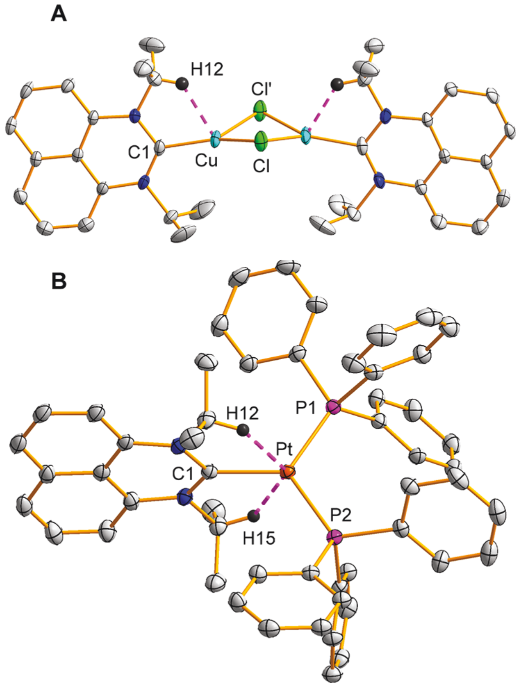


Figure 3. Solid-state structures of (A) $[(C_{10}H_6({}^{i}PrN)_2C)CuCl]_2$, **3**, and (B) $(C_{10}H_6({}^{i}PrN)_2C)Pt(PPh_3)_2$, **4**. Cyan, orange, blue, gray, green, and pink ellipsoids (50% probability) represent copper, platinum, nitrogen, carbon, chlorine, and phosphorus, respectively. Hydrogen atoms are omitted for clarity unless necessary to display close interatomic interactions (dark gray spheres). A benzene solvent molecule was removed for clarity for **3**. Selected bond lengths (Å) and angles (deg): 3 Cu−C1, 1.932(3); Cu−Cl, 2.263(1); Cu−Cl′, 2.391(1); C1−Cu−Cl, 140.91(12); C1−Cu−Cl′, 123.81(12); Cl1−Cu−Cl′, 94.91(4); 4 Pt−C1, 2.057(3); Pt−P1, 2.2475(9); Pt−P2, 2.2581(9); C1−Pt−P1, 121.20(8); C1−Pt−P2, 124.69(8); P1−Pt−P2, 113.92(3).

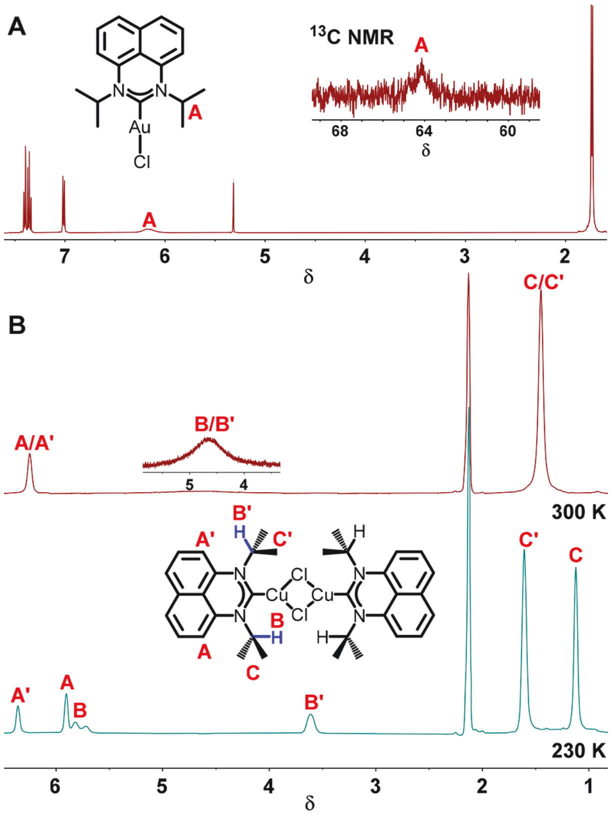


Figure 4. ^{1}H NMR spectra of (A) $(C_{10}H_6({}^{i}PrN)_2C)AuCl$, **1**, in CD_2Cl_2 shown with partial ^{13}C NMR inset. Methine proton and carbon resonances are severely broadened suggesting slow rotation about the C−N bond. (B) $[(C_{10}H_6({}^{i}PrN)_2C)CuCl]_2$, **3**, in C_7D_8 shown at two temperatures, 300 K (top) and 230 K (bottom).

carbons in the ^{13}C NMR for **1** are also significantly broadened to where they are barely visible above the baseline at 64.24 ppm (Figure 4A, inset). The carbene resonance is visible at 192.89 ppm (Figure S2). These observations are consistent with reports of the NMRs of complexes that employed the same perimidine-based NHC.[28−30] The silver complex, **2**, shows a less pronounced downfield shift (4.81 ppm) for the methine protons that is also significantly broadened (Figure S5). Notably, neither the methine carbons nor the carbene carbon were observed in the ^{13}C NMR (Figure S6). Their absence is due to the splitting of the two spin active isotopes of silver which often make observation of carbons near the metal challenging.[66] HSQC measurements for **2** also could not resolve the methine carbon resonance.

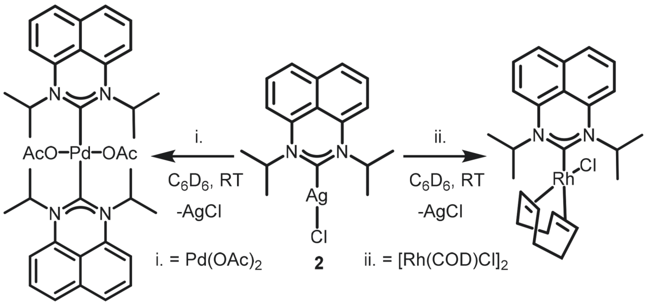
The isopropyl groups on the solid-state structure for $[(C_{10}H_6(^{i}PrN)_2C)CuCl]_2$ (**3**) are in different conformations. If this is true in solution, then there would be separate resonances for their protons. However, a ^{1}H NMR at room temperature revealed a spectrum similar to **2** (Figure 4B), with broad singlets at 4.64 and 1.40 ppm. Cooling the solution to 230 K in toluene-d_8 revealed the resonances for the isopropyl diverge to two distinct sets of peaks (Figures 4B and S13 for COSY). Consequently, we conducted a detailed variable-temperature ^{1}H NMR study between 245 and 330 K in 5 K increments (Figure S12). The coalescence temperature was found to be 270 K, which gives a calculated rotation energy barrier for the isopropyl moiety of 12.4 kcal/mol.[67,68] Finally, the carbene resonance for **3** is observed in the ^{13}C NMR at 197.68 ppm (Figure S9).

The NMR for platinum complex **4** was distinct from the group 11 complexes (**1**−**3**) due to the additional phosphine ligands. A single phosphorus resonance with Pt satellites was observed at 45.6 ppm in the ^{31}P NMR (Figure S19). More notably, complex **4** was the only d^{10} complex that was synthesized that showed the expected septet coupling on the methine proton at 6.84 ppm in the ^{1}H NMR (Figure S16). The sharp peaks on the isopropyl resonances demonstrate that the isopropyl groups rotate freely at room temperature even though there are close contacts observed in the solid-state structure. Finally, all expected carbon resonances were observed in the ^{13}C NMR (or HSQC) except the carbene resonance. We attribute the lack of observable signal for the carbene due to additional splitting from the phosphines and platinum which divides an already typically weak signal.

Although the free carbene, $(C_{10}H_6(^{i}PrN)_2C)$, can be prepared under air-free conditions, it is often more convenient to employ silver NHC transmetalation reagents.[69−72] To our knowledge, there have been no reported transmetalation reactions with this class of NHC. We tested the ability of **2** to transmetalate the NHC to form known complexes (Scheme 2). Reacting $(C_{10}H_6(^{i}PrN)_2C)AgCl$ (**2**) in deuterated benzene with $Pd(OAc)_2$ immediately led to the formation of a gray solid (AgCl). After 2 h, ^{1}H NMR confirmed the formation of previously reported $(C_{10}H_6(^{i}PrN)_2C)_2Pd(OAc)_2$ in 55% yield versus an internal standard, which is similar to the yield achieved from the free carbene method.[30] An analogous reaction with $[Rh(COD)Cl]_2$ and **2** yielded the product $(C_{10}H_6(^{i}PrN)_2C)Rh(COD)Cl$ in 62% yield in only 1 h based on integration versus an internal standard.[29]

In conclusion, we have synthesized the first NHC d^{10} complexes with a perimidine scaffold, including the first noble metal examples. The copper complex is also the first example of this motif on a first-row transition metal. All four complexes were characterized by single-crystal X-ray diffraction, and the gold and silver complexes yielded linear geometries, while the platinum complex is trigonal planar. The copper complex forms a dimer with bridging chlorides in the solid state. All four complexes showed close contacts with methine protons in the solid state, and these interactions were confirmed in solution by ^{1}H NMR which revealed downfield resonances, a lack of splitting, and severe broadening. Low-temperature NMR confirmed that for the copper complex, the isopropyl moieties can be prevented from rotating freely. Finally, the silver complex is an effective transmetalation reagent to transfer this NHC to palladium and rhodium. Transmetalation is an effective strategy for forming NHC complexes, so this outcome can expand the breadth of perimidine-based NHC chemistry beyond the few metals on the periodic table studied to date.

Scheme 2. Transmetalation Reactions from 2



■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.1c00189.

Experimental details, NMR, MS, and additional spectra (PDF)

Accession Codes

CCDC 2074103−2074106 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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Notes

The authors declare no competing financial interest.

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