ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

Mild, Safe, and Versatile Reagents for $(CF_2)_n$ Transfer and the Construction of Fluoroalkyl-Containing Rings

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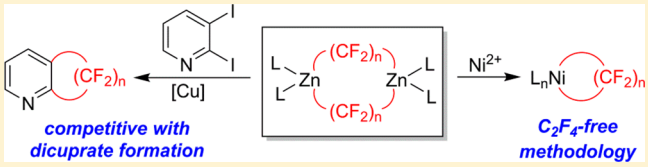
Supporting Information

ABSTRACT: The preparation of new dizinc reagents $[(MeCN)_2Zn((CF_2)_n)_2Zn(MeCN)_2]$ (n = 3, 4, and 6) is reported. We show that the C4 reagent can readily transmetalate nickel to form a mononuclear perfluoronickelacycle. We also demonstrate that the reagents can be used to prepare novel fluoroorganics containing either perfluoroalkyl ring systems or perfluoroalkyl linked arenes under relatively mild conditions.

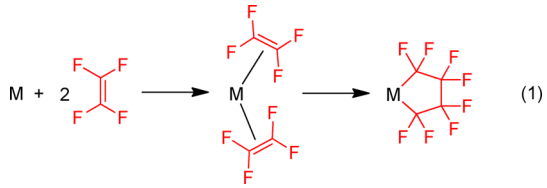


INTRODUCTION

Molecules and materials that contain sequential difluoromethylene groups are becoming increasingly important in industry today. Repeating difluoromethylene groups can be found in a diverse array of products, such as fluorinated refrigerants, pharmaceuticals, pesticides, surfactants, polymers, liquid crystals, anesthetics, blood substitutes, aerosol formulations, and lubricants.[1−27] While methods for incorporating perfluoroalkyl, difluoromethyl, fluoromethyl, and isolated difluoromethylene groups have advanced significantly in recent years,[28] reagents that can systematically incorporate repeating difluoromethylene groups of various sizes have been slower to develop. Radical-based reagents, which have their own limitations, are perhaps the most successful synthons for such functionalities to date.[29−33]

The $(CF_2)_n$ functionality is also of interest to the synthetic organic and organometallic communities as it is the backbone of perfluoroalkyl-based metallacycles, the largest numbering class of which are the perfluorometallacyclopentanes. Perfluorometallacyclopentanes like those shown in Chart 1 have been known since 1961.[34−53] Stone and co-workers prepared the first example (**1**) involving the reaction of iron pentacarbonyl with tetrafluoroethylene (TFE). They found that the resulting metallacycle was extraordinarily stable and failed to release carbon monoxide or fluorocarbon even after being treated with bromine for 60 h at 50 °C.[38] Such thermal stability contrasts that seen for nonfluorinated iron carbonyl metallacycle derivatives, which have been implicated as intermediates in cyclopentanone formation.[54,55]

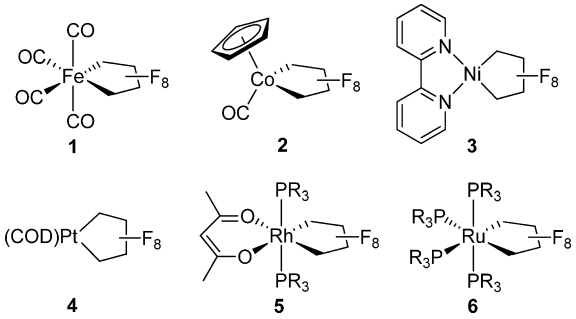
To our knowledge, the synthetic routes to well-defined perfluorometallacyclopentanes all involve the oxidative coupling of TFE, as outlined in eq 1.[35,36,38,42−44,46,49,52,53,56] This



(1)

oxidative coupling reaction appears to be common for other late transition metals, as complexes **2**−**6** (Chart 1) are all formed upon reaction of an appropriate metal precursor with TFE. Such routes are problematic for discovery research today as TFE has become increasingly unavailable for purchase due to the explosion hazards associated with its handing.[57−65] TFE can be prepared inexpensively on a reasonable scale from the thermal pyrolysis of waste polytetrafluoroethylene (PTFE),[66−69] but such routes typically involve temperatures above 600 °C and the use of a quartz furnace connected to a vacuum manifold. Moreover, the pyrolysis route does not eliminate the detonation hazards accompanying the recondensed TFE or the problems associated with the acute toxicity of octofluoroisobutylene,[70−77] which can be formed as a byproduct in the thermal degradation of PTFE.[68,78,79] Other methods exist to generate TFE more expensively on a small

Chart 1. Selected Known Examples of Perfluorometallacyclopentanes



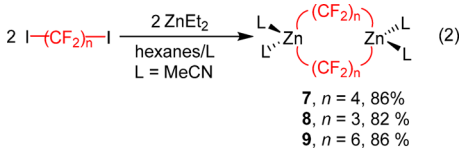
Received: October 17, 2013
Published: November 18, 2013

   dx.doi.org/10.1021/om401016k | *Organometallics* 2013, 32, 7552−7558

scale,[80,81] but require gas handling techniques that can complicate experimental protocols.

RESULTS AND DISCUSSION

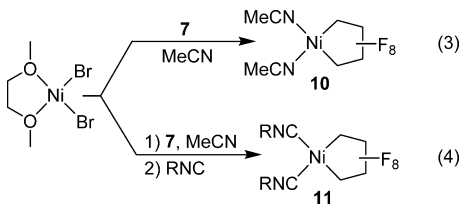
To circumvent the use of TFE in preparing perfluorometallacyclopentanes, we sought to develop a new reagent that could directly install a C_4F_8 group onto a metal precursor. In particular, we wanted access to a difunctionalized perfluorobutane that could be used as a transmetalating agent. Naumann and co-workers found that bis(*n*-perfluoroalkyl)zinc complexes could be prepared by reacting diethyl zinc with 2 equiv of *n*-perfluoroalkyl iodide.[82,83] We imagined that a difunctionalized zinc derivative could also be prepared using this method if 1,4-diiodooctafluorobutane was used as the fluorinated substrate, as described in eq 2. A dinuclear structure



could be anticipated based on the work of Bickelhaupt with nonfluorinated congeners.[84] Indeed, upon addition of acetonitrile to a stirred mixture of 1,4-diiodooctafluorobutane and diethyl zinc in hexanes, a white precipitate formed, which, by X-ray crystallography, was confirmed to be complex **7** (Figure 1).

The method to prepare the bifunctionalized fluoroalkylzinc reagents is general for other diiodoperfluoroalkanes, as rings both smaller and larger than **7** can be prepared (eq 2). A crystal structure of **8** has also been obtained (Figure 1) and confirms its dinuclearity. Complex **8** is notable because this reagent can potentially be used to prepare perfluorometallacyclobutanes, which may be used to study and develop the yet unknown perfluoroalkene metatheses reaction. The only example of a perfluorometallacyclobutane reported to date was that synthesized by Karel and co-workers[41] and was generated by decarbonylation of $[(CO)_4Fe(COCF_2CF_2CF_2)]$. The zinc complex **8** is expected to provide entries to a diverse class of new perfluorometallacyclobutanes through convenient transmetalation approaches.

The zinc complexes **7**–**9** were observed to slowly lose $HF_2C–(CF_2)_n–CF_2H$ upon dissolution in organic solvents. The loss of $HF_2C–(CF_2)_n–CF_2H$ was even observed after monitoring the ^{19}F NMR spectra of the zinc reagents *before* the introduction of coordinating solvent. Nevertheless, the reagents can effectively be used as CF_2 transfer agents if handled properly. For instance, complex **7** reacts readily with the nickel precursor $[(DME)NiBr_2]$, as described in eq 3, to afford the



mononuclear metallacyclic complex **10** in 84% yield. A crystal structure of **10** has been obtained (Figure 2), and the data confirm that a monomeric nickel complex is produced. Complex **10** represents a metallacyclic version of the recently prepared $[(MeCN)_2Ni(R_f)_2]$ complexes, which are convenient

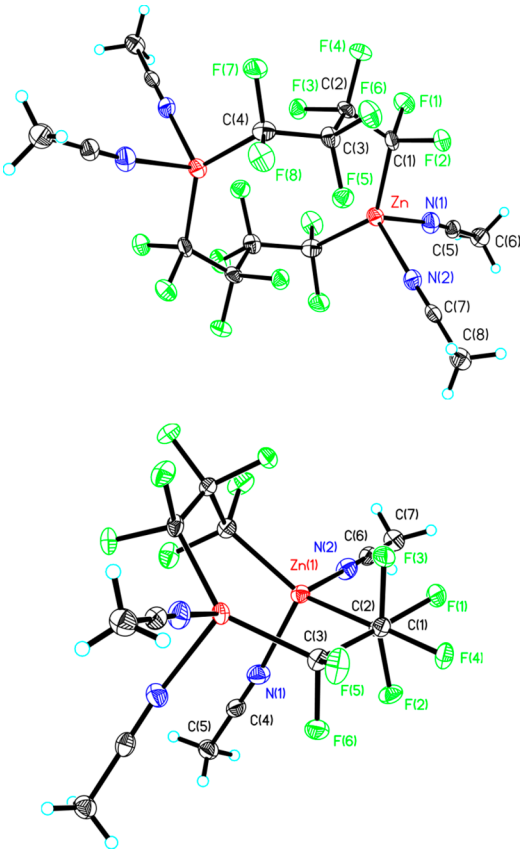


Figure 1. Top: ORTEP diagram of **7**. Selected bond lengths (Å): Zn–C1 2.032(4); Zn–C4 2.036(5); Zn–N2 2.077(4); Zn–N1 2.102(4). Selected bond angles (deg): C1–Zn–C4 134.44(17); C1–Zn–N2 106.98(15); C4–Zn–N2 110.04(16); C1–Zn–N1 105.24(16); C4–Zn–N1 96.14(17); N2–Zn–N1 96.37(14). Bottom: ORTEP diagram of **8**. The co-crystallized benzene has been omitted for clarity. Selected bond lengths (Å): Zn1–C1 2.0248 (17); Zn1–N1 2.0835(16); Z1–N2 2.1161(15). Selected bond angles (deg): C1–Zn1–N1 105.63(6); C1–Zn1–N2 100.74(6); N1–Zn1–N2 93.86(6).

precursors to a variety of $[LNi(R_f)_2]$ derivatives.[85] Indeed, repeating the transmetalation in the presence of other coligands, such as 2,6-dimethylphenyl isocyanide, leads to the formation of **11** in 73% yield. Complex **11** has also been structurally characterized, and selected bond lengths and angles are provided in Figure 2.

Having established that the zinc reagents can be used as effective transmetalating agents for nickel, we sought to provide preliminary results for functionalizing organic diiodides to novel organofluorine ring systems. Perfluoroalkyl zinc reagents are known to be able to transmetalate copper to afford active perfluoroalkylating agents,[86,87] but there have been no reports of ring-forming reactions using this methodology. In studies using the new zinc reagents **7**–**9**, we found that the variation in fluoroalkyl chain length of the zinc reagents led to dramatic differences in reactivity toward organic diiodides. For example, the C_3 zinc derivative **8** reacted cleanly with aryl diiodides in the presence of CuCl/1,10-phenanthroline to afford the fluoroalkyl ring-containing structures **12** and **13** (eq 5) in 46% and 93% yields, respectively. The higher yields obtained with the more activated substrates like 2,3-diiodopyridine is not unknown with zinc reagents. Kremlev and co-workers found that $[(DMF)_2Zn(CF_3)_2]$ in combination with CuBr could trifluoromethylate 2-iodopyridine in 93% yield, whereas

dx.doi.org/10.1021/om401016k | *Organometallics* 2013, 32, 7552–7558

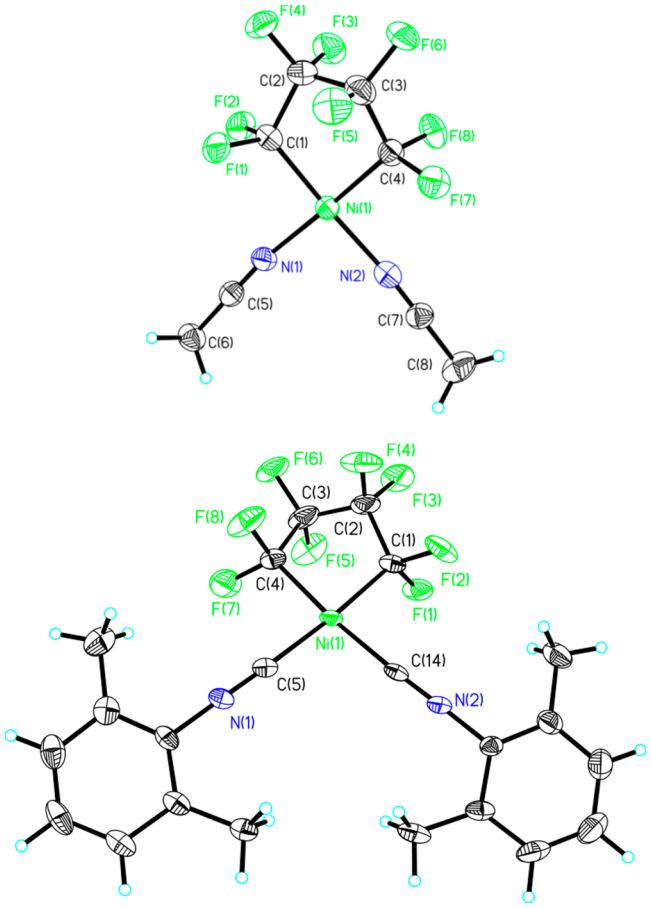
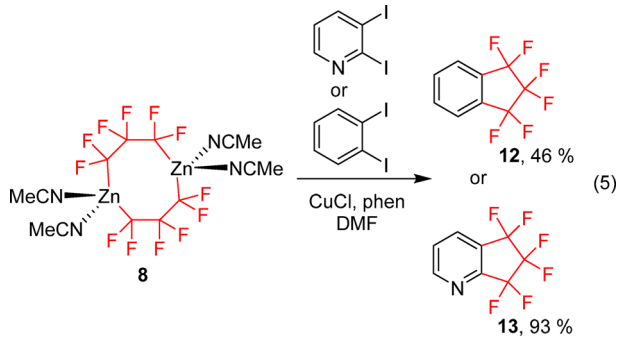
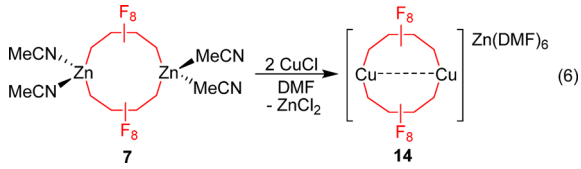


Figure 2. Top: ORTEP diagram of **10**. Selected bond lengths (Å): Ni1−C1 1.893(5); Ni1−C4 1.887(5); Ni1−N1 1.903(5); Ni1−N2 1.898(5). Selected bond angles (deg): C4−Ni1−C1 86.7(2); C4−Ni1−N2 91.5(2); C1−Ni1−N2 176.8(2); C4−Ni1−N1 177.7(2); C1−Ni1−N1 91.3(2). Bottom: ORTEP diagram of **11**. Selected bond lengths (Å): Ni1−C5 1.870(5); Ni1−C14 1.870(4); Ni1−C4 1.933(5); Ni1−C1 1.937(4); C5−N1 1.158(6); C14−N2 1.155(6). Selected bond angles (deg): C5−Ni1−C14 97.13(18); C5−Ni1−C4 89.52(19); C14−Ni1−C4 172.79(18); C5−Ni1−C1 175.51(19); C14−Ni1−C1 87.36(19); C4−Ni1−C1 86.0(2); N1−C5−Ni1 176.1(4); N2−C14−Ni1 173.7(4).



reactions with aromatics containing electron-donating groups like methyl or methoxy only afforded the trifluoromethyl products in 2−4% yield.[86] Similar, but suboptimal, yields for the reaction described in eq 5 could be obtained if ligandless CuCl was used as the copper source.

Surprisingly, when the C_4 zinc derivative **7** was used to perform similar perfluoroalkylation reactions with copper, only trace amounts of ring-containing products could be detected. To determine the nature of the problem with the C_4 derivative, we explored whether or not the transmetalation of the perfluoroalkyl group from zinc to copper was occurring. In fact, mixing 4 equiv of CuCl with **7** in DMF led almost instantaneously to the formation of a new species by ^{19}F NMR spectroscopy, with resonances appearing at δ −115.8 and −139.5. We have determined by X-ray crystallography that this new species is the unusual bis-cuprate **14** (eq 6, Figure 3).



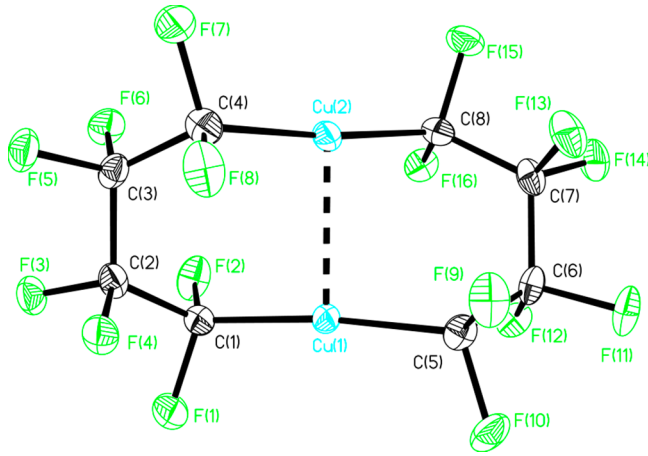


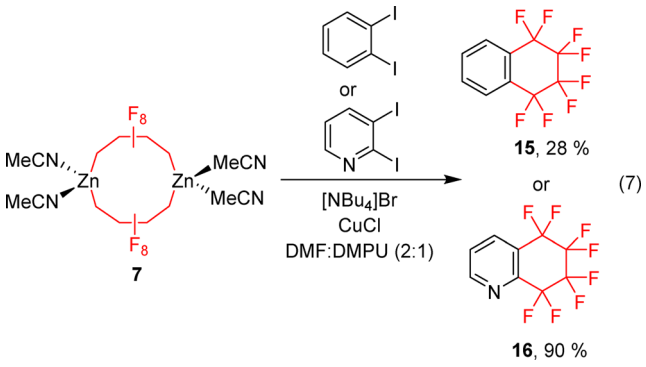
Figure 3. ORTEP diagram of the dicuprate **14**. The $[Zn(DMF)_6]$ dication has been removed for clarity. Selected bond lengths (Å): Cu1−C1 1.925(2); Cu1−C5 1.925(2); Cu1−Cu2 2.5481(4); Cu2−C8 1.927(2); Cu2−C4 1.934(2). Selected bond angles (deg): C1−Cu1−C5 173.67(9); C8−Cu2−C4 174.21(9).

Complex **14** is only the second bisperfluoroalkyl cuprate to be structurally characterized[88] and is the only such one that has a dicopper and dianionic core. Isolation of **14** allowed us to study its reactivity with aryl diiodides, and importantly, it was determined that this bis-cuprate species is *inactive* in ring-forming perfluoroalkylation reactions.

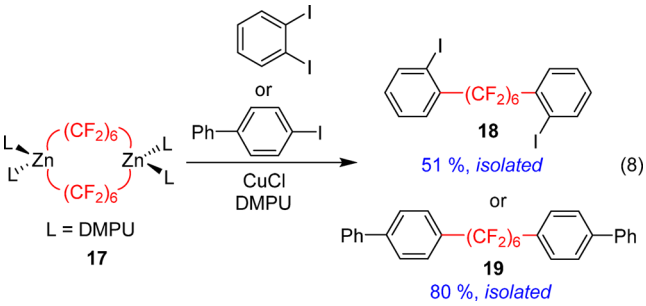
In attempts to achieve successful perfluoroalkylations with **7** by avoiding the formation of **14**, we explored the effect of additives. We found that addition of $[NBu_4]Br$ and DMPU (DMPU = 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone) to zinc complex **7** *before* the introduction of copper to the mixture indeed allowed access to the fluoroalkylated products **15** and **16** (eq 7). As of yet, we do not fully understand the mechanism by which these additives help the reaction progress, although Organ and co-workers noted that bromide may generate higher-order zincate complexes that are effective transmetalating agents in certain Negishi reactions.[89] Interestingly, the use of $[NBu_4]Br$ does not appear to influence the reactivity of the C_3 or the C_6 zinc reagents.

We observed that the C_6 zinc reagent, under conditions screened thus far, does not lead to the formation of perfluoroalkyl ring systems. However, reaction conditions may be optimized to produced perfluoroalkyl linked arenes such as **18** and **19** in moderate to good isolated yields (eq 8).

dx.doi.org/10.1021/om401016k | *Organometallics* 2013, 32, 7552−7558



Crystal structures of **18** and **19** have been obtained, and the ORTEP diagrams are shown in Figure 4.



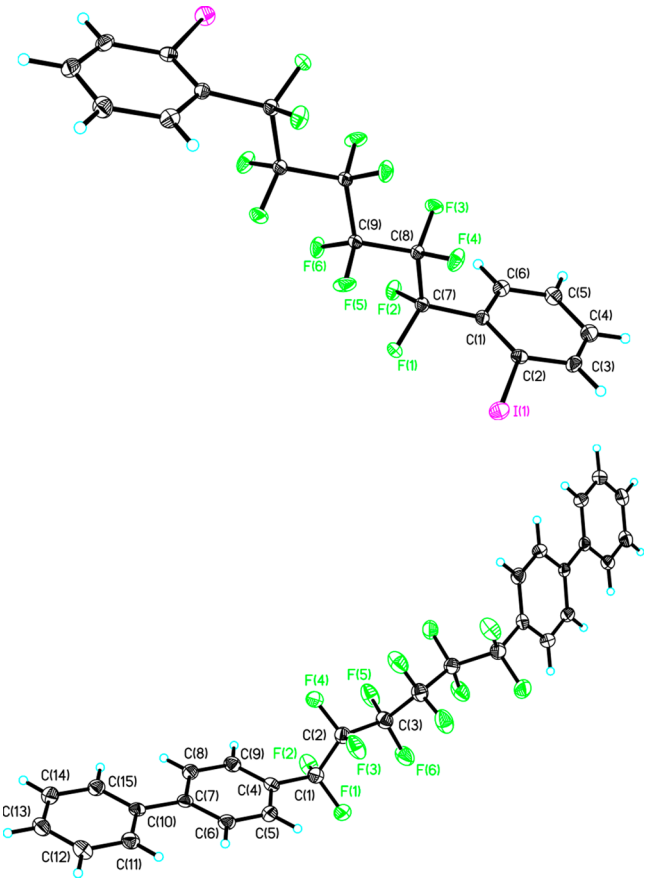


Figure 4. ORTEP diagrams of **18** (top) and **19** (bottom). Experimental bond lengths and angles are provided in the Supporting Information.

The above reactions demonstrate that the new zinc reagents described herein not only may be used to transmetalate nickel but also may be used to generate perfluoroalkyl-based organic ring systems and perfluoroalkyl linkers. Importantly, there have been few reports to date of methods to prepare fused aryl/fluoroalkyl ring systems of variable size. The most versatile system we have found was that reported by Chen and coworkers[90,91] in which $Cl(CF_2)_nI$ is first coupled to aryl iodides using a superstoichiometric amount of copper metal to afford $Ar\text{-}(CF_2)_nCl$. These $Ar\text{-}(CF_2)_nCl$ products then undergo intramolecular radical cyclizations upon reaction with $Na_2S_2O_4$ to afford fused ring systems. The method we are reporting here is a complementary one that not only can form fused ring systems under mild nonradical conditions but also can be used to prepare transition-metal fluoroalkyl metallacycles for developing potentially more sophisticated organometallic transformations. The exploration of such transformations is currently being pursued in our laboratories.

CONCLUSIONS

In summary, a simple protocol to prepare bis(perfluoroalkyl)-metallacyclic dizinc reagents has been established.[92] The new zinc reagents are bifunctionalized perfluoroalkyl groups that may be used to transmetalate other metals and thereby transfer the chain of repeating difluoromethylene groups. Given the importance of transmetalation reactions in synthetic chemistry, these new reagents can foreseeably be used in a variety of transformations to install repeating difluoromethylene units in both small and large molecules. Moreover, the reagent that we demonstrated that could be used to prepare a perfluorometallacyclopentane is anticipated to be helpful to smaller laboratories that are less-equipped for generating and handling perfluorinated gases, such as TFE, in order to study the fundamental chemistry involving perfluorometallacyclopentanes.

EXPERIMENTAL PROCEDURES

General Considerations. All manipulations were performed using standard Schlenk and high-vacuum techniques or in a nitrogen-filled glovebox. Solvents were purified by passing through activated alumina and/or copper in a solvent purification system supplied by Pure Process Technology. 1,4-Diiodooctafluorobutane and 1,6-diiodododecafluorohexane were purchased from SynQuest Laboratories, Inc. and used without further purification. 1,3-Diiodohexafluoropropane was prepared according to a previously published procedure.[93] Solution ^1H NMR spectra were recorded at ambient temperature on a Bruker DRX 500 MHz spectrometer and referenced to residual proton solvent signals. ^{13}C NMR spectra were recorded on a Bruker NMR spectrometer operating at 125 MHz and referenced to solvent signals. ^{19}F spectra were recorded on the Bruker NMR spectrometer operating at 470 MHz. A Bruker D8 Quest diffractometer was used for X-ray crystal structure determinations. Mass spectral data were recorded on a HP 5890 Series II Plus GC/MS.

Preparation of $[(MeCN)_2Zn((CF_2)_4)_2Zn(MeCN)_2]$ (7). An 8 mL portion of a 1.0 M diethyl zinc solution in hexanes was prechilled in a vial to −78 °C under a nitrogen atmosphere. 1,4-Diiodooctafluorobutane (3.64 g, 8 mmol) was diluted with 8 mL of pentane and was also prechilled to −78 °C. The zinc solution was then added dropwise to the 1,4-diiodooctafluorobutane solution at −78 °C. The reaction vial was then stirred for 3 h at −20 °C. After 3 h, 4 mL of MeCN was then added and the mixture was stirred vigorously for 1 h and then warmed to room temperature. The pentane layer was decanted away, and benzene was added to precipitate an off-white solid. The mixture was stirred overnight, and then the solid was pumped dry on a high-vacuum line. The product 7 was obtained in 86% yield as a white solid.

dx.doi.org/10.1021/om401016k | Organometallics 2013, 32, 7552−7558

^{19}F NMR (CD_3CN, 470 MHz): δ −125.5 (br s), −125.8 (br s). Anal. Calcd (found) for $C_{16}H_{12}F_{16}N_4Zn_2$: C, 27.65 (27.76); H, 1.74 (1.88). The C_4F_8 zinc derivative decomposes slowly in the solution state but is stable in the solid state.

Preparation of [(MeCN)$_2$Zn((CF$_2$)$_3$)$_2$Zn(MeCN)$_2$] (8). A volume of 5 mL (5.00 mmol) of a 1.0 M diethyl zinc solution in hexanes was added to a prechilled vial (−78 °C) under a nitrogen atmosphere and diluted with 5 mL of pentane. A mass of 2 g (5 mmol) of 1,3-diiodohexafluoropropane was added slowly, and the whole solution was stirred in a nitrogen-filled glovebox cold well at −78 °C for 8 h and gradually warmed to room temperature. Then 4 mL of acetonitrile was added at room temperature and the mixture was stirred for 12 h. After decanting the top pentane/hexane layer, 10 mL of diethyl ether was added to the acetonitrile layer, and the whole solution was put in the fridge in a glovebox (−35 °C) for recrystallization. The white crystals were collected by filtration, and they were dried on a high-vacuum line overnight to give an 82% product yield. ^{19}F NMR (CD_3CN, 470 MHz): δ −126.2 (s), −136.8 (s). Anal. Calcd (found) for $C_{14}H_{12}F_{12}N_4Zn_2$: C, 28.26 (28.29); H, 2.03 (2.32).

Preparation of [(MeCN)$_2$Zn((CF$_2$)$_6$)$_2$Zn(MeCN)$_2$] (9). A 4 mL portion of a 1.0 M solution of $ZnEt_2$ in hexanes was transferred into an empty vial, diluted with 4 mL of pentane, and cooled to −78 °C. In another vial, 4 mmol (2.206 g) of diiodododecafluorohexane was dissolved into 4 mL of pentane. The diiodododecafluorohexane solution was then added dropwise to the $ZnEt_2$ solution at −78 °C and then stirred for 3 h at −20 °C. Then 4 mL of acetonitrile was added dropwise to the solution. The resulting mixture was left to stir vigorously overnight at room temperature. The solution was pumped dry for 2 days on a high-vacuum line, yielding an off-white powder (86%). ^{19}F NMR (CD_3CN, 470 MHz): δ −122.1 (br s), −123.0 (br s). −123.3 (br s). Anal. Calcd (found) for $C_{20}H_{12}F_{24}N_4Zn_2$: C, 26.84 (26.97); H, 1.35 (1.39).

Preparation of [(MeCN)$_2$Ni(C$_4$F$_8$)] (10). Zinc complex 7 (251 mg, 0.32 mmol), freshly crystallized from benzene, was dissolved in 8 mL of MeCN and was then immediately added dropwise to a stirred mixture of [(DME)$NiBr_2$] (202 mg, 0.65 mmol) in 4 mL of acetonitrile. The mixture was stirred for 3 h at room temperature, and then the volatiles were removed under vacuum. The nickel complex was extracted from the residue with benzene, and this benzene solution was filtered and then dried under vacuum to yield an orange solid. Yield of **10**: 84%. X-ray quality crystals were grown from THF/ether. ^{19}F NMR (CD_3CN, 470 MHz): δ −106.0 (s), −139.4 (s). Anal. Calcd (found) for $C_8H_6F_8N_2Ni$: C, 28.19 (27.85); H, 1.77 (1.88).

Preparation of [(2,6-Dimethylphenyl isocyanide)$_2$Ni(C$_4$F$_8$)] (11). [(MeCN)$_2$Ni(C_2F_4)] (**10**) (131 mg, 0.38 mmol) was dissolved in 10 mL of THF, and then 110 mg (0.83 mmol) of 2,6-dimethylphenyl isocyanide was immediately added. The mixture was stirred for 3 h at room temperature, and then the volatiles were removed under vacuum. The nickel complex was washed with pentane and pumped dry under vacuum to yield a yellow solid. 73% yield. ^{1}H NMR (toluene-d_8, 500 MHz): δ 6.60 (t, J = 7.6, 1H), 6.40 (d, J = 7.6, 2H), 1.87 (s, 6H). ^{19}F NMR (THF, 470 MHz): δ −100.1 (s, 2F), −139.3 (s, 2F). Anal. Calcd (found) for $C_{22}H_{18}F_8N_2Ni$: C, 50.71 (50.92); H, 3.48 (3.58).

Preparation of 1,1,2,2,3,3-Hexafluoro-2,3-dihydro-1*H*-indene (12) and 5,5,6,6,7,7-Hexafluoro-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine (13). Copper(I) chloride (10 mg, 0.1 mmol) and 1,10-phenanthroline (18 mg, 0.1 mmol) were dissolved in 1 mL DMF, and the solution was stirred for 30 min at room temperature. Zinc complex **8** (30 mg, 0.05 mmol) and 1,2-diiodobenzene (32 mg, 0.1 mmol) were added to the solution, and the whole mixture was transferred to a J-Young NMR tube, sealed, and heated to 90 °C for 16 h. NMR yields were based on trifluorotoluene as an internal standard: 46% yield for **12**. ^{19}F NMR (470 MHz, $CDCl_3$) δ −108.45 (t, J = 5.0 Hz, 4F), −133.05 (quint, J = 4.3 Hz, 2F). EI MS: m/z = 226. Compond **13** was prepared in an analogous manner (yield: 93%). ^{19}F NMR (470 MHz, MeCN-d_3): δ −108.21 (s, 2F), −114.44 (s, 2F), −132.19 (quint, J = 4.3 Hz, 2F). EI MS: m/z = 227.

Isolation of Dicuprate Complex 14 for Structural Characterization. The zinc complex 7 (1.05 g, 1.51 mmol) and copper chloride (300 mg, 3.03 mmol) were dissolved in 4 mL of DMF and stirred for 3 h at room temperature. The mixture was checked by ^{19}F NMR, and it was determined that 63.3% conversion to the cuprate species occurred. The mixture was filtered through a 0.2 μm PTFE filter, and the yellow solution was placed in a vial. Ether was layered on top of the yellow solution and placed in a −35 °C freezer overnight to form colorless crystals. ^{19}F NMR (DMF-d_7, 470 MHz): δ −115.75 (br s, 4F), −139.48 (br s, 4f). Crystals decompose upon extended time under vacuum. Anal. Calcd (found) for $C_{26}H_{42}Cu_2F_{16}N_6O_6Zn$: C, 30.29 (29.72); H, 4.11 (4.01).

Preparation of 1,1,2,2,3,3,4,4-Octafluoro-1,2,3,4-tetrahydronaphthalene (15). The zinc complex 7 (34.75 mg, 0.05 mmol) was dissolved in 0.8 mL of DMF and 0.4 mL of DMPU. Tetra-*n*-butylammonium bromide (32.24 mg, 0.10 mmol) was then added, followed by sequential addition of copper chloride (9.9 mg, 0.10 mmol) and 1,2-diiodobenzene (32.99 mg, 0.10 mmol). A 0.012 mL portion of trifluorotoluene (0.098 mmol) was syringed into the vial as the internal standard. The solution was then transferred to a J-Young NMR tube, sealed, and heated for 3 h at 100 °C. The NMR yield of **15** was 28%. ^{19}F NMR (ethyl ether, 470 MHz): δ −103.6 (br s, 4F), −135.7 (br s, 4F). EI MS: m/z = 276.

Preparation of 5,5,6,6,7,7,8,8-Octafluoro-5,6,7,8-tetrahydroquinoline (16). The zinc complex 7 (34.8 mg, 0.05 mmol) was weighed into in a 20 mL vial and dissolved in 0.8 mL of DMF. Tetra-*n*-butylammonium bromide (32.24 mg, 0.10 mmol) was added, followed by the addition of copper chloride (9.9 mg, 0.10 mmol) and 2,3-diiodopyridine (33.09 mg, 0.10 mmol). A 0.012 mL portion of trifluorotoluene (0.098 mmol) was syringed into the vial as the internal standard. The solution was transferred to a J-Young NMR tube, sealed, and then heated for 3 h at 100 °C. The NMR yield of **16** was 90%. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.05 (d, J = 4.7 Hz, 1H), 8.23 (d, J = 8.2 Hz, 1H), 7.76 (dd, J = 8.2, 4.7 Hz, 1H). ^{19}F NMR ($CDCl_3$, 470 MHz): δ −105.9 (s, 2F), −111.6 (s, 2F), −135.6 (s, 2F), −136.0 (s, 2F). EI MS: m/z = 277.

Preparation of 17. A 4 mL portion of a 1.0 M solution of $ZnEt_2$ in hexanes was transferred into an empty vial, diluted with 4 mL of pentane, and cooled to −78 °C under a nitrogen atmosphere. In another vial, 4 mmol (2.2160 g) of diiodododecafluorohexane was dissolved into 4 mL of pentane. The diiodododecafluorohexane solution was then added dropwise to the $ZnEt_2$ solution at −78 °C and then stirred overnight at room temperature. A 2 mL portion of DMPU was then added dropwise to the solution. The resulting mixture was left to stir vigorously overnight at room temperature. After removing the pentane layer, the product was precipitated from the solution by slowly adding 8 mL of Et_2O. Filtration and evaporation on a high-vacuum line afforded **17** (2.3017 g, 92%) as a white solid. ^{19}F NMR (471 MHz, DMF-d_7): δ −121.42, −123.55, −124.79. Anal. Calcd (found) for $C_{36}H_{48}F_{24}N_8O_4Zn_2$: C, 34.77 (34.19); H, 3.89 (3.89).

Preparation of 18. To a resealable pressure tube were added [(DMPU)$_2$Zn((CF$_2$)$_6$)$_2$Zn(DMPU)$_2$] (62.4 mg, 0.05 mmol), CuCl (19.9 mg, 0.2 mmol), diiodobenzene (99.0 mg, 0.3 mmol), and DMPU (1 mL) sequentially in a glovebox at room temperature. The resulting mixture was sealed and quickly submerged in an oil bath preheated to 110 °C. After 19 h, the mixture was cooled to room temperature and purified by chromatography on silica gel (eluent: *n*-hexane/ethyl acetate = 1/0 to 20/1) to afford 2,2′-(perfluorohexane-1,6-diyl)bis(iodobenzene) (36.0 mg, 51%, white solid). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.09 (d, J = 7.85 Hz, 1H), 7.58 (d, J = 7.85 Hz, 1H), 7.48 (t, J = 7.85 Hz, 1H), 7.19 (t, J = 7.74 Hz, 1H). ^{19}F NMR ($CDCl_3$, 470 MHz): δ −107.1 (s), −119.8 (s), −122.4 (s). Anal. Calcd (found) for $C_{18}H_8F_{12}I_2$: C, 30.62 (30.72); H, 1.14 (1.22).

Preparation of 19. To a resealable pressure tube were added [(DMPU)$_2$Zn((CF$_2$)$_6$)$_2$Zn(DMPU)$_2$] (62.1 mg, 0.05 mmol), CuCl (19.7 mg, 0.2 mmol), 4-iodo-1,1′-biphenyl (56.2 mg, 0.2 mmol), and DMPU (1 mL) sequentially in a glovebox at room temperature. The resulting mixture was sealed and quickly submerged in an oil bath preheated to 110 °C. After 17 h, the mixture was cooled to room temperature and purified by chromatography on silica gel (eluent: *n*-

dx.doi.org/10.1021/om401016k | *Organometallics* 2013, 32, 7552−7558

hexane/ethyl acetate = 1/0 to 20/1) to afford 4,4″-(perfluorohexane-1,6-diyl)di-1,1′-biphenyl (48.5 mg, 80%): white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (t, J = 7.3 Hz, 2H), 7.48 (t, J = 8.0 Hz, 4H), 7.62 (d, J = 7.0 Hz, 4H), 7.67 (d, J = 8.4 Hz, 4H), 7.71 (d, J = 8.2 Hz 4 H). ^{19}F NMR (471 MHz, $CDCl_3$): δ −111.48, −122.26, −122.79.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic information files (CIF) and selected NMR spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

D.A.V. thanks the Office of Basic Energy Sciences of the U.S. Department of Energy (DE-FG02-13ER16369) for support of this work. Dedicated to Professor William D. Jones on the occasion of his 60th birthday.

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