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Synthesis of a perfluoroalkyl-substituted α-diimine by Sm-mediated reductive coupling

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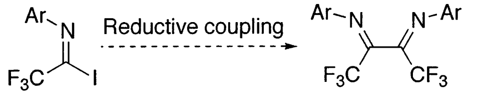
Abstract—Samarium iodide mediates the reductive coupling of imidoyl iodide **1** to the corresponding enediamine **2**, which is oxidized by manganese dioxide to an *N*,*N'*-diaryl-α-diimine **3**. Single-crystal X-ray diffraction analysis shows that **2** crystallizes in the *E*,*E*-geometry, with a substantial nonplanarity of the N=C–C=N moiety, allowing a π-stacking interaction between the *N*-aryl rings. Unlike its 2,3-dimethyl analogue, **3** resists formation of chelates with palladium(II) or platinum(II).

In recent years, α-diimine (1,4-diazabutadiene) ligands have played an important role in late transition metal chemistry, particularly in the development of olefin polymerization catalysts,[1] and in the study of C–H bond activation.[2] An attractive feature of this ligand set is the tunability of its steric and electronic properties: a wide variety of α-diimines may be prepared by condensation reactions of anilines with 1,2-diones. The substituents on the imine carbons are generally hydrogen or methyl groups.[3] Although the incorporation of perfluoroalkyl groups in these positions has been reported recently,[4] metal complexes of these diimines have not yet been described.

We were interested in preparing highly electron-withdrawing α-diimine ligands for the study of C–H bond activation by late transition metals. An increase in the electrophilicity attainable in late metal α-diimine complexes would also be of interest in polymerization catalysts. We have synthesized and structurally characterized an α-diimine bearing trifluoromethyl groups on the ligand backbone and on the *N*-aryl rings; however, the desired metal complexes remain elusive.

The precursor to trifluoromethyl-substituted α-diimines through aniline condensation would be 1,1,1,4,4,4-hexafluoro-2,3-butanedione, prepared from 2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene by oxidation with chromium trioxide in fuming sulfuric acid.[5] Curiously, the only reported condensations of anilines with this dione appear to be cyclizations, in which the dione reacts with diamines to form aromatic heterocycle moieties.[6]

Imidoyl halides derived from perfluoroalkanoic acids have been the subject of considerable research by Uneyama and co-workers.[4a,7–9] Preparative routes to the chlorides, bromides and iodides have been described, and numerous combinations of *N*-aryl group and perfluoroalkyl substituent are known.[7] These halides have shown utility in cross-coupling and radical reactions,[8] and as precursors to metal imidoyl derivatives, which can be used as masked perfluoroacyl anions.[9] Recently, a palladium-catalyzed homocoupling, using CO as the reducing agent, was reported; this method affords a flexible route to the desired α-diimines (Eq. (1)).[4a]



(1)

We had been investigating the use of a stoichiometric metal-based reducing agent to achieve this reaction, for which some precedent existed. Imidoyl halides derived from benzoic acid have been reductively coupled by low-valent manganese[10a,b] complexes, but the product diimines are obtained in very low yields; a nickel-mediated procedure achieves yields up to 50%, but requires the use of hazardous nickel tetracarbonyl as starting material.[10c] In contrast, the analogous coupling of benzoyl chloride to benzil, proceeding through an enediol

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Keywords: imidoyl halides; reductive coupling; samarium(II); perfluoroalkyl; α-diimines.

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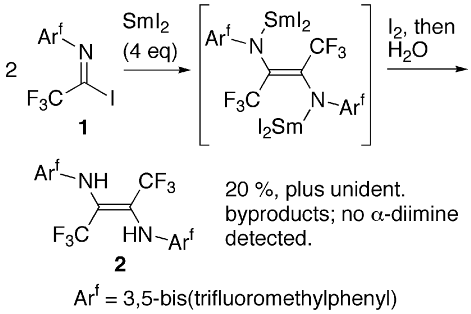
which subsequently air-oxidizes, is easily accomplished using samarium(II) iodide.[10d]

In a preliminary experiment (Scheme 1), *N*-[3,5-bis-(trifluoromethyl)phenyl] trifluoroacetimidoyl iodide (**1**)[11] was added to a solution of SmI_2 (2.4 equiv.) in THF at −40°C. The deep blue color of the samarium reagent soon faded, leaving a dark red–brown mixture. Based on the stoichiometry, the immediate product was expected to be the bis[Sm(III)] derivative of the enediamine, and it was hoped that oxidation with I_2 at −78°C would afford the diimine and SmI_3. TLC and ^{19}F NMR analysis of the crude oxidation product showed a complex mixture of products; however, enediamine **2** could be isolated as a colorless solid, in low yield (20%), by column chromatography on silica gel. The ^{19}F NMR spectrum of **2** in CD_2Cl_2 displays a singlet resonance for the four aryl-CF_3 groups at −63.7 ppm, and a singlet for the two backbone CF_3 groups at −64.3 ppm.[12a] The ^{1}H NMR spectrum, in addition to the expected aryl protons, displays a singlet, integrating to two protons, at 6.2 ppm.[12b] Oxidation of **2** with MnO_2 suspension in CH_2Cl_2 affords pale yellow α-diimine **3**, in which the backbone CF_3 groups give rise to a singlet at −68.1 ppm in the ^{19}F NMR spectrum (the chemical shift of the aryl-CF_3 groups is unchanged), and the N–H resonance of the ^{1}H NMR spectrum has disappeared.

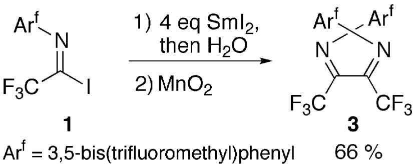


Scheme 1.

Other routes to perfluoroalkyl-substituted α-diimines were also explored. Imidoyllithium reagents, generated from the iodides by halogen-metal exchange, react with a variety of electrophiles.[9a,b] Dimerization of imidoyllithium derivatives to give dilithiated enediamines has been reported to occur in up to 50% yield. Specific experimental details are lacking, however (this was apparently an undesired side reaction), and we have been unable to isolate enediamine **2** from **1**, or to convert the *N*-(2,6-xylyl) analogue of **1** to an enediamine, under these conditions.

The Sm(II)-mediated reductive coupling was repeated on larger scale, replacing the ineffective oxidative quench with an aqueous workup; enediamine **2** was isolated in crude form and, without further purification, subjected to oxidation by MnO_2 (Scheme 2). Removal of the manganese oxides by filtration, concentration, and recrystallization of the residual solid from hexanes at −20°C afforded **3** as pale yellow crystals in 66% yield based on imidoyl iodide (Scheme 2).[13]

Slow recrystallization of **3** from CH_2Cl_2/pentane afforded crystals suitable for X-ray diffraction analysis.[14] Diimine **3** crystallizes in the $P\bar{1}$ (#2) space group, with two molecules in the triclinic unit cell. The structure (Fig. 1) confirms the identity of the product, and shows the imine groups in the *E*,*E*-geometry, opposite to that needed to chelate a metal center. The dihedral



Scheme 2.

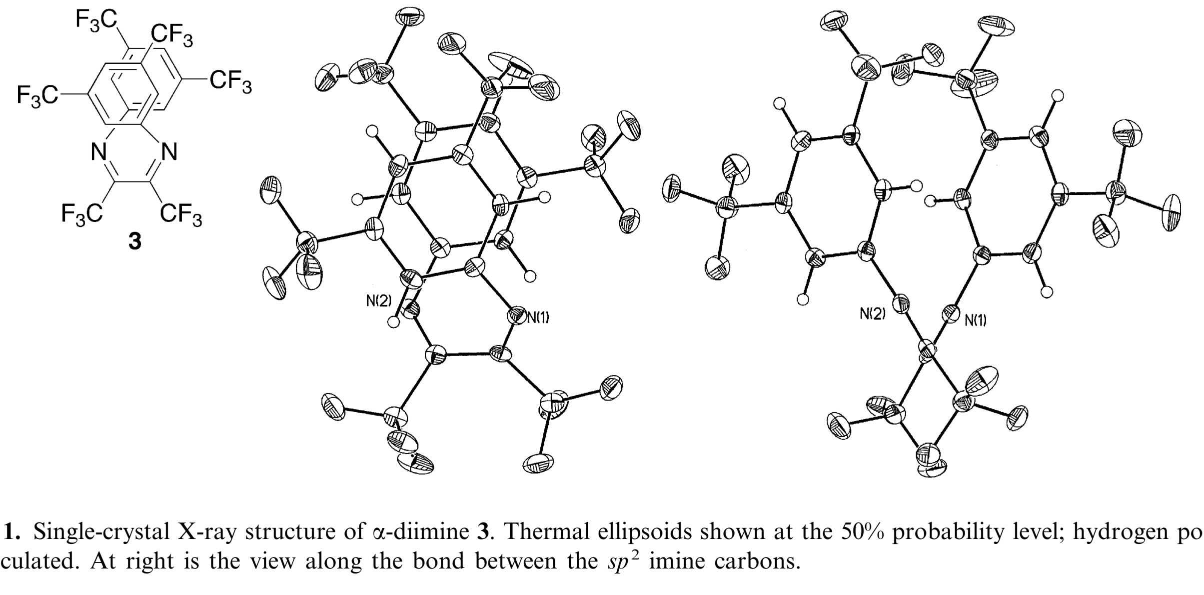


Figure 1. Single-crystal X-ray structure of α-diimine **3**. Thermal ellipsoids shown at the 50% probability level; hydrogen positions are calculated. At right is the view along the bond between the sp^2 imine carbons.

angle between the imine groups is large, at 59.1(3)°, diminishing the steric interactions between the backbone CF_3 groups and allowing a π-stacked arrangement of the aryl groups. The aryl rings form an angle of 12.36(3)°, opening away from the diimine backbone; the centroid of the first ring is 3.356 Å out of the plane of the second phenyl ring, and the centroid of the second is 3.415 Å from the plane of the first phenyl ring.

The attempted reaction of **3** with (COD)Pd(CH_3)Cl or with (COD)Pd$(CH_3)_2$, which are known to metallate *N*,*N*-diaryl-2,3-dimethyl-1,4-diazabutadienes,[1a] failed to yield a chelated palladium complex. At temperatures where the palladium precursors were stable, no reaction was observed by ^1H or ^{19}F NMR, whereas at higher temperatures, decomposition to metallic palladium and free ligand was observed. The reaction of **3** with bis-[dimethylplatinum-(μ-dimethyl sulfide)], under conditions known to metallate the 2,3-dimethyl analogue of **3**,[2a] was similarly unsuccessful, with no reaction observed at 0°C, and deposition of a Pt mirror observed after stirring overnight at room temperature.

We wondered whether **3** was inherently difficult to metallate due to its geometry, in which both imine moieties must isomerize, and the π-stacking between the aryl rings must be disrupted, before chelation can occur. A search for this structural feature in α-diimine ligands, however, revealed that *N*,*N′*-diphenyl-9,10-phenanthrenequinone-diimine exists in this geometry both in the solid state and in solution.[15] Its crystal structure, in fact, is closely analogous to that of **3**, with a dihedral angle of 51.3° between the imine moieties, and a π-stacking interaction, with similar angles and distances, between the phenyl rings. The quinonediimine, however, metallates quite readily, by reaction with $(PhCN)_2PdCl_2$ in CH_2Cl_2 solution (Fig. 2).

Under these conditions, **3** did not form a palladium complex. Instead, precipitation of $PdCl_2$ occurred, leaving free benzonitrile and **3** in solution. In the presence of excess benzonitrile (4 equiv.), the solutions remained homogeneous, but no reaction occurred as judged by ^{19}F NMR. Generally, attempted metallations with Pd or Pt dihalide complexes resulted in precipitation of the parent dihalides in nonpolar solvents, no reaction in polar aprotic solvents, and reduction to the metal by ethereal or alcohol solvents at elevated temperatures. We speculate that, although the geometry of the starting diimine does not by itself preclude metallation, the imine lone pairs are poorly nucleophilic due to the inductive effect of the CF_3 groups, and so the coordination of one imine may form an intermediate too short-lived to permit the necessary imine isomerization, and chelation, to occur.

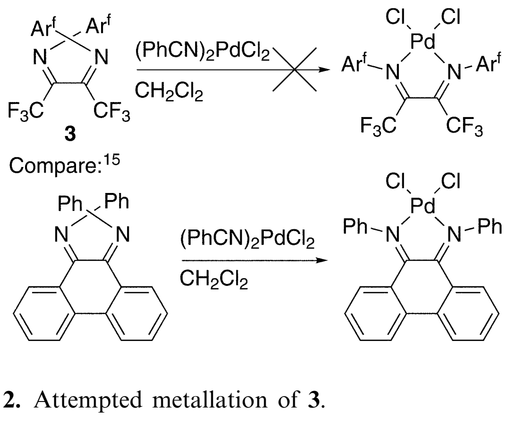


Figure 2. Attempted metallation of **3**.

Given the strong π-acidity expected for this diimine, we thought that perhaps complexation would occur more readily with a more electron-rich metal center. No reaction occurred between **3** and $Pd_2(dba)_3$ (dba = 1,3-dibenzylideneacetone) in C_6D_6 solution at room temperature, and on heating to 80°C, the sample rapidly deposited a palladium mirror. However, dissolution of **3** (ca. 1.3 equiv.) with $Pd(PPh_3)_4$ in C_6D_6 under Ar resulted in an immediate color change, with the formation of a clear red solution.

The ^{19}F NMR spectrum of this solution showed, in addition to excess **3**, two new singlets for the backbone CF_3 moieties at −58.8 and −60.6 ppm (each integrating to 3F), and two singlets at −62.5 and −62.9 ppm for the aryl-CF_3 groups (6F each).[12a] The ^{31}P NMR spectrum shows two doublets, arising from two inequivalent phosphines (25.6 ppm and 21.4 ppm; $^2J = 33$ Hz), and a singlet for free PPh_3 (−4.6 ppm; 2 equiv.).[12c] Thus, a new complex has apparently formed, but the inequivalent phosphine ligands and imine moieties indicate an asymmetric binding mode, possibly the coordination of one imine as an η^2 ligand (Fig. 3).

In conclusion, we have synthesized an *N*,*N*-diaryl α-diimine bearing trifluoromethyl groups on both the imine carbons and on the *N*-aryl groups. The synthetic route, mediated by samarium diiodide, is a preparatively useful reductive coupling of an imidoyl halide. The resulting α-diimine crystallizes in the *E*,*E*-geometry, and so far resists formation of chelate complexes of palladium and platinum.

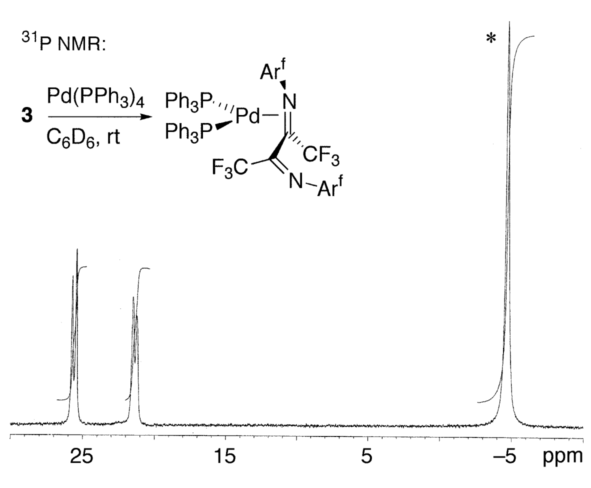


Figure 3. ^{31}P NMR spectrum, and possible structure, of $\mathbf{3}\cdot Pd(PPh_3)_2$. * = free PPh_3.

Acknowledgements

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11. The general literature procedure (Ref. 7) involves the reaction of an anilines with a perfluoroalkanoic acid, triethylamine, and triphenylphosphine in carbon tetrachloride, producing the imidoyl chloride in one-pot. Halide exchange with sodium iodide in acetone produces the imidoyl iodide. We found it more convenient to treat the *N*-aryltrifluoroacetamide with diiodotriphenylphosphorane (prepared in situ from triphenylphosphine and iodine) and triethylamine in dichloromethane; imidoyl iodide **1** was obtained in 93% yield. This modification avoids the use of carbon tetrachloride, and allows purification of the product by simple vacuum distillation rather than column chromatography.
12. All NMR spectra were measured using a Varian Mercury 300 spectrometer. (a) ^{19}F NMR spectra were obtained at 282.4 MHz, and referenced with respect to external $CFCl_3$. (b) ^{1}H NMR spectra were obtained at 300.1 MHz and referenced with respect to residual solvent. (c) ^{31}P NMR spectra were obtained at 121.5 MHz and referenced with respect to external 85% aqueous H_3PO_4.
13. **Preparation of α-diimine 3**: Imidoyl iodide **1** (0.56 mL, 2.33 mmol) was added dropwise, via syringe, to a stirred solution of SmI_2 in THF (Aldrich, 0.1M, 60 mL, 6.0 mmol) at −50°C, in a Schlenk flask under Ar. Within a minute, the deep blue–green solution began to turn red–brown. The reaction mixture was allowed to warm to −30°C over 20 min, then cooled to −40°C. A mixture of water and THF (50/50 v/v, 10 mL) was added via cannula. The resulting suspension was stirred for 5 min, then the flask was opened and brine (50 mL) was added. The layers were separated, and the aqueous phase was extracted with Et_2O (3×25 mL). The combined organic portions were dried over $MgSO_4$, filtered and concentrated in vacuo. The red–brown residual solid was taken up in CH_2Cl_2 (10 mL), and added via pipette to a stirred, ice-cold suspension of MnO_2 in CH_2Cl_2 (10 mL). The resulting mixture was stirred for 4 h, with warming to room temp, then filtered through Celite and concentrated in vacuo. Recrystallization of the resulting light orange solid from hexanes, followed by trituration with cold CH_2Cl_2 (2×1 mL), afforded **3** as pale yellow crystals, 0.476 g (66%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.82 (s, 2H), 6.98 (s, 4H); ^{19}F NMR (282 MHz, CD_2Cl_2) δ −63.7 (s, 12F), −68.1 (s, 6F).
14. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 180092. These data can be obtained via http://www.ccdc.cam.ac.uk/conts/retrieving.html, free of charge (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk). Structure factors are available from the authors via e-mail: xray@caltech.edu.
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