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Practical synthesis of ferrocenyldiarylstibines and bismuthines

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The reaction of *in situ*-generated lithioferrocene with pnictines EAr_3 (E = Sb and Bi, Ar = aryl) is presented as a reliable, robust, and practical approach for synthesising ferrocenyldiarylstibines and bismuthines. In addition to simple derivatives $FcEAr_2$ (Fc = ferrocenyl), the method enables the preparation of functional derivatives, thereby opening access to P,Sb and P,Bi-hybrids.

Compared with their very practically successful phosphine counterparts,[1] ferrocene derivatives bearing heavier pnictogen donor substituents have received only limited attention thus far.[2] This may be attributed to their lower chemical stability, reflecting weaker E–C bonds, difficulties associated with their preparation, and the widely held notion that heavier pnictines are only phosphine analogues.[3] The lack of data on these compounds prompted us to explore the reactivity and coordination behaviour of distibine **1**[4] as the antimony analogue of the extensively studied ferrocene-based diphosphine 1,1′-bis(diphenylphosphino)ferrocene (dppf)[5] and the related P, Sb-hybrid compounds **2**,[6] **3**,[7] and **4** (Scheme 1).[8]

As a part of our studies focused on heavier ferrocene-based pnictines, we tried to devise an alternative and potentially general synthetic route that could expand the scope of the accessible compounds or simplify their synthesis. The currently available methods are typically based on conventional metathesis reactions between lithiated intermediates and suitable pnictine halides R_nEX_{3-n}[9] or, less often, rely on catalytic approaches that also employ R_nEX_{3-n} or the corresponding organometallic derivatives (*e.g.*, stannanes).[10] However, these starting materials are not always easily accessible.

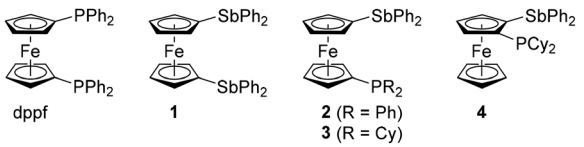
Recently, Krempner *et al.*[11] reported that organic superbases efficiently catalyse the replacement of pentafluorophenyl groups in stibines $Sb(C_6F_5)_nPh_{3-n}$ (n = 1–3) with various CH acids. This reaction formally proceeds under proton transfer from the stronger CH acid to the C_6F_5 group. Inspired by this work, we suggest that lithioferrocenes (as much stronger bases) could react even with much more accessible triarylstibines possessing less acidic aryl groups and that this reaction could be extended to the other elements in group 15.

During our initial reaction tests, we investigated the interactions of *in situ*-generated lithioferrocene (FcLi; Fc = ferrocenyl) with pnictines EPh_3 (E = P-Bi; 1 equiv.). While no reactions were observed for triphenylphosphine and triphenylarsine (the details are provided in the SI), the corresponding stibine and bismuthine were smoothly converted to their respective monosubstituted ferrocenes, $FcEPh_2$ (E = Sb, **5**; E = Bi, **6**; see Scheme 2). The yields of the target ferrocenylpnictines did not change dramatically when the amount of EPh_3 was increased to 2 equiv. For instance, during the preparation of **5**, 45% and 58% NMR yields were obtained when 1 or 2 equiv. of $SbPh_3$ were employed, respectively. In some cases, however, the use of more EPh_3 was beneficial, increasing the product yield and making the target products easier to isolate from the reaction mixture because of the lower amount of side products (presumably Fc_2EPh) formed.

An NMR analysis of the mixture obtained by adding $SbPh_3$ to FcLi and quenching it with methanol revealed resonances that were attributable to $FcSbPh_2$ and unsubstituted ferrocene arising from the protonolysis of FcLi. Additionally, signals of *n*-butylbenzene, presumably formed by the coupling of *n*-butylbromide and LiPh, were also detected. The process can be thus formally described as follows:

$$FcBr + Li\textit{n}\text{-}Bu \rightarrow FcLi + \textit{n}\text{-}BuBr,$$

$$FcLi + SbPh_3 \rightarrow FcSbPh_2\ (Fc_2SbPh) + LiPh.$$



Scheme 1 Dppf, its Sb analogue, and the related phosphinostibines (Cy = cyclohexyl).

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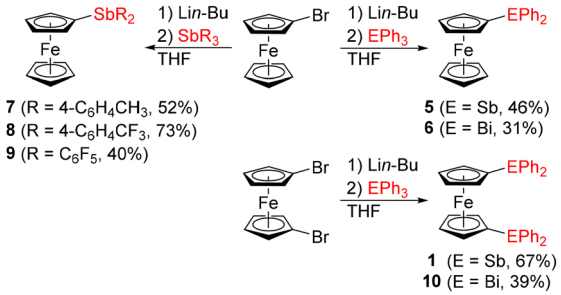
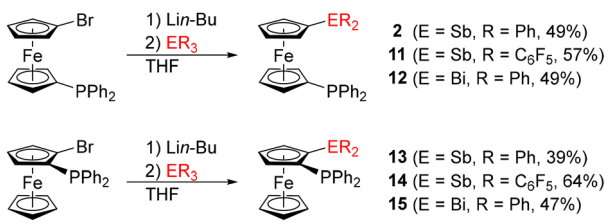


Scheme 2 Synthesis of ferrocenyldiarylpnictnines and bispnictines (the isolated yields of recrystallised products are given in parentheses).

The reactions of FcLi with stibines $Sb(C_6H_4R\text{-}4)_3$ (R = Me, CF_3) and $Sb(C_6F_5)_3$ proceeded equally well, producing the respective stibines **7–9**. Furthermore, 1,1′-dilithioferrocene, generated *in situ* from 1,1′-dibromoferrocene and *n*-butyllithium, could be converted to the symmetrical dipnictines **1** and **10** (Scheme 2), which were isolated in 67% and 39% yields, respectively. In contrast, no reaction was observed with tricyclohexylstibine ($SbCy_3$). $SbCy_3$ may not have entered the pnictinyl group transfer reaction owing to the higher basicity of the respective alkyllithium (CyLi) relative to that of FcLi, which represents a limitation of the proposed approach.[12]

To expand the potential accessible compounds, we explored the reactions of $SbPh_3$, $Sb(C_6F_5)_3$, and $BiPh_3$ with a nonisolated lithioferrocene resulting from 1′-(diphenylphosphino)-1-bromoferrocene. Interestingly, these reactions also proceeded smoothly under Li/Sb and Li/Bi exchanges, affording hybrid phosphines **2**, **11**, and **12** in good yields (Scheme 3). The planar chiral, isomeric compounds **13–15** were obtained similarly using racemic 2-(diphenylphosphino)-1-bromoferrocene as the starting material.

All the compounds were fully characterised using spectroscopic methods (NMR and MS), and their bulk purity was confirmed by elemental analysis. The electrochemical properties of the compounds were examined *via* cyclic voltammetry (for details, see the SI). All the compounds displayed reversible oxidations attributable to the ferrocene/ferrocenium redox transition. The trend in the redox potentials suggested that the electron-withdrawing characteristic of the pnictine substituents decreases from PPh_2 through $SbPh_2$ to $BiPh_2$ (Fig. 1) and that the latter group has virtually no influence on the redox potential of the ferrocene/ferrocenium couple (the redox



Scheme 3 Synthesis of ferrocene-based phosphinostibines and bismuthines (the isolated yields of recrystallised products are given in parentheses).

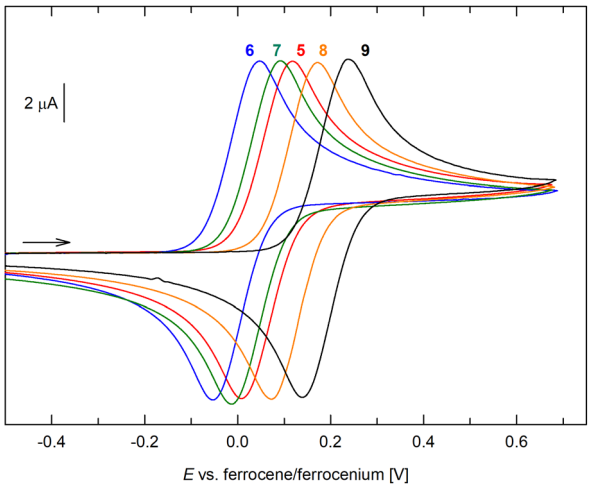


Fig. 1 Representative cyclic voltammograms of monopnictine derivatives **5–9** ($c \approx 0.1$ mM, scanning rate: 100 mV s^{-1}, Pt disc electrode, 0.1 M *n*-$Bu_4N[PF_6]/CH_2Cl_2$). For complete data, see the SI.

potential determined for **6** and **10** was practically the same as that of ferrocene itself). It also indicated that the electronic effect of the aryl group is transferred onto the ferrocene unit.

In addition, the crystal structures of all the new compounds were determined by single-crystal X-ray diffraction analysis (Fig. 2 and SI). For dipnictines **12**, **13**, and **15**, the analysis provided relatively poor results because of positional disorder at the pnictine groups, which could not be fully resolved. The crystal packing of the dipnictines was apparently controlled by the overall molecular shape, and the differences between the homologous pnictogen substituents were not sufficient for differentiating between these groups in the crystal state[6] (*N.B.* this problem was not observed for compounds **11** and **14** bearing different substituents at the Sb and P atoms; Fig. 2). To diminish the tendency toward disorder, the "problematic"

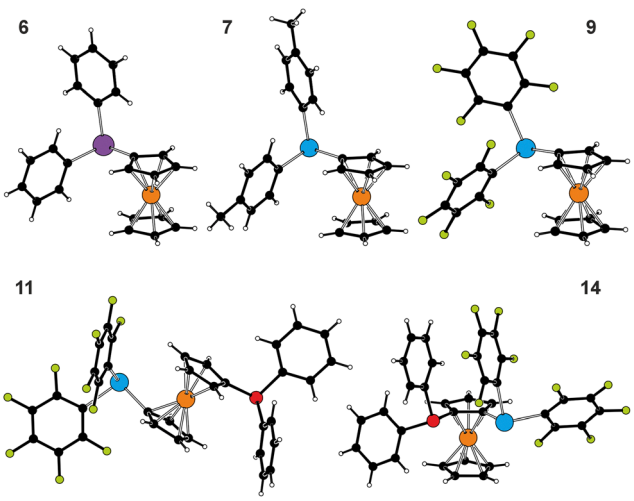
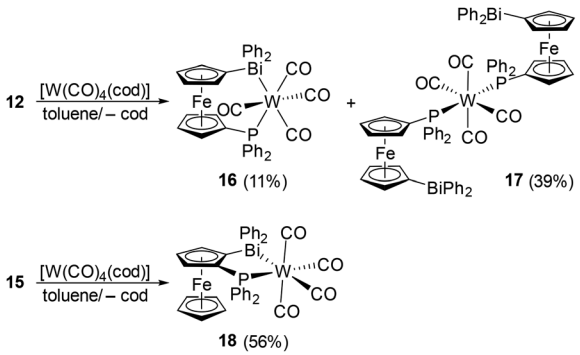


Fig. 2 Molecular structures of representative pnictines **6**, **7**, and **9** and the pair of isomeric ditopic derivatives **11** and **14** (colours used: C – black, H – white, Fe – orange, Sb – cyan, Bi – violet, P – red, and F – yellow–green). For complete structural diagrams and geometric parameters, see the SI.



Scheme 4 Reactions of isomeric phosphinobismuthines **12** and **15** with $[W(CO)_4(cod)]$ (cod = cycloocta-1,5-diene; isolated yields in parentheses) and the molecular structure of complex **18**.

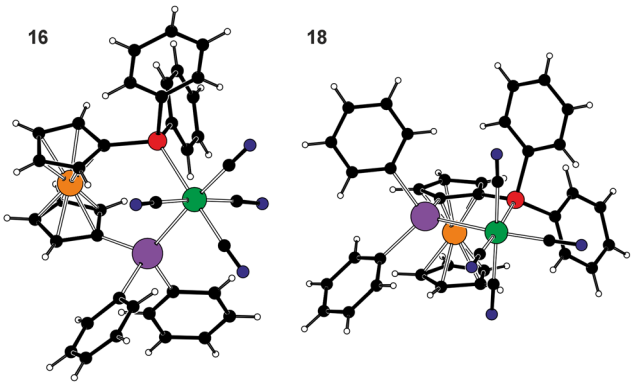


Fig. 3 Molecular structures of **16** and **18**·$\frac{1}{2}C_6H_{14}$ (molecule 1; colours used: C – black, H – white, Fe – orange, Sb – cyan, Bi – violet, P – red, O – blue, and W – green). Selected distances and angles (in Å and deg, respectively) for **16**: W–Bi 2.7991(6), W–P 2.542(2), and P–W–Bi 92.21(5); for **18**: W–Bi 2.800(7), W–P 2.511(2), and P–W–Bi 81.56(6). For **16**, only one orientation of the disordered phenyl ring is shown, and the solvent molecule in the structure of **18**·$\frac{1}{2}C_6H_{14}$ has been omitted for clarity.

compounds were desymmetrised *via* reactions with $BH_3{\cdot}SMe_2$, which produced the corresponding phosphine–borane adducts **12**·BH_3, **13**·BH_3, and **15**·BH_3 in high yields (see the SI). Adducts with Sb- and Bi-substituents acting as Lewis bases were not detected even when the BH_3 source was used in excess; this finding was in line with the lower basicity of the heavier pnictines, as corroborated by the calculated methyl cation affinities (MCAs;[13] see the SI).

The coordination behaviour of phosphinobismuthines **12** and **15** as new hybrid ferrocenylphosphines[1] was preliminarily assessed through reactions with $[W(CO)_4(cod)]$ (cod = cycloocta-1,5-diene). Thus, the reaction with **12** in hot toluene (Scheme 4) proceeded under the formation of four compounds, from which complexes **16** and **17** could be isolated and characterised (see the SI for details). An analogous reaction involving **15** proceeded more selectively to produce chelate complex **18**, with a 56% yield following chromatography. Overall, the observed reactivity is consistent with the weaker coordination of the bismuthine moiety and the presence of a relatively loose chelate ring in **16**. Compared with **12**, compound **15** produced a more stable (rigid) chelate and thus reacted more selectively.

The molecular structures of **16** and **18**·$\frac{1}{2}C_6H_{14}$ (Fig. 3) revealed an undistorted octahedral coordination sphere around the tungsten atom, albeit the individual W–C and C–O distances differed because of the dissimilar π-acceptor properties of the ligands (CO > P, Bi; see the SI for more details).

Chelate coordination of the phosphinobismuthines in **16** and **18** also enabled a comparison between the donor properties of the two homologous pnictine donor groups (relative to that of the CO reference groups). An analysis conducted *via* the intrinsic bond orbital (IBO)[14] approach revealed that the phosphine moiety behaved as a stronger σ donor compared to the bismuthine moiety. As π acceptors, however, both pnictine groups were considerably less π-acidic than the CO ligands (see the SI).[15]

In summary, we developed a robust and practical method for synthesising ferrocenyldiarylstibines and bismuthines. This method is based on the redistribution reactions between lithioferrocenes and homoleptic pnictines ER_3 and obviates the use of the often difficult-to-access halopnictines R_nEX_{3-n} as starting materials. The reaction appears to be governed by the relative basicity of the organic groups involved in the process. Moreover, the general reactivity exhibited by the pnictine series corresponds with the trend of the E–C bond energies, which decrease along the group from N to Bi[16] (no reaction was observed with PPh_3 and $AsPh_3$ having relatively stronger E–C bonds; *vide supra*).

The general applicability of the developed synthetic protocol was demonstrated by the successful preparation of simple and hybrid pnictine derivatives, including both known (**1**, **2**, and **5**) and previously unreported (all others) compounds. More generally, the method can be used to synthesise new related compounds, thereby facilitating explorations of the chemical properties of the neglected stibines and bismuthines and their P,E-hybrid counterparts (E = Sb and Bi, respectively), which are becoming increasingly important owing to the specific reactivity exerted by the different pnictine groups and catalytic properties.[17]

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Conflicts of interest

There are no conflicts of interest to declare.

Data availability

The data supporting this article have been included as a part of the supplementary information (SI). Supplementary information: experimental details, crystallographic data and structural diagrams; results from the electrochemical measurements and

DFT calculations; and copies of the NMR spectra. See DOI: https://doi.org/10.1039/d5cc05762k.

CCDC 2491409–2491421 contain the supplementary crystallographic data for this paper.[18a–m]

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