Phosphoramidate-mediated conversion of metal carbonyls into metal isonitriles

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The reaction of metal carbonyls with readily-available phosphoramidate anions provides a new route to metal isonitriles; in particular, enantiomerically pure isonitrile complexes are easily accessed by this method.

Our recent interest in tricarbonyl(vinylketene)iron(0) complexes and their nitrogen analogues, tricarbonyl(vinylketenimine)iron(0) complexes, led us to devise a method for the conversion of the former into the latter, central to which were the anions of diethyl *N*-alkylphosphoramidates.[1] We subsequently questioned whether or not this approach could be used to convert metal carbonyls into metal isonitriles, a transformation worthy of investigation in view of the ubiquity of carbonyl and isonitrile ligands in organometallic chemistry.

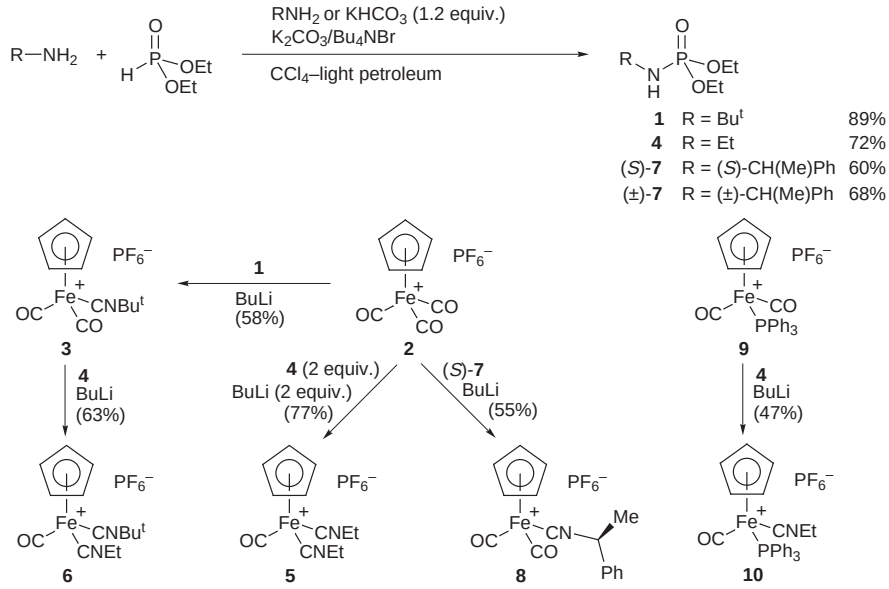
We report herein our preliminary results in this area which reveal that the phosphoramidate-mediated conversion of metal carbonyls to metal isonitriles is indeed a viable process. The reaction's potential may be summarised by the following points: (i) unlike the 'classical' carbonyl–isonitrile exchange approach to isonitrile ligands[2] the process avoids the use of 'free' isonitriles, compounds which are frequently volatile, smelly and toxic; (ii) the method introduces isonitrile ligands in a controlled manner, again in contrast to the 'classical' carbonyl–isonitrile exchange reaction which frequently delivers mixtures of products;[3] (iii) phosphoramidates are easy to synthesise[4] and handle;‡ and (iv) the method provides rapid access to non-racemic chiral isonitrile ligands, a class of ligand which has received remarkably little attention to date.§

An initial experiment was carried out using phosphoramidate **1** and the tricarbonyliron cation **2**. Phosphoramidate **1** was synthesised by stirring together 2.2 equiv. of *tert*-butylamine and 1.0 equiv. of diethyl phosphite in CCl_4–light petroleum according to literature precedent;[4a,c] work-up gave **1** as a colourless stable liquid in 89% yield (Scheme 1). The iron cation **2** was synthesised from $[(C_5H_5)(CO)_2Fe]_2$ by reduction with sodium amalgam, and sequential addition of ethyl chloroformate, hydrogen chloride and ammonim hexafluorophosphate.[8] This produced cation **2** in 81% overall yield as an orange–yellow crystalline solid.

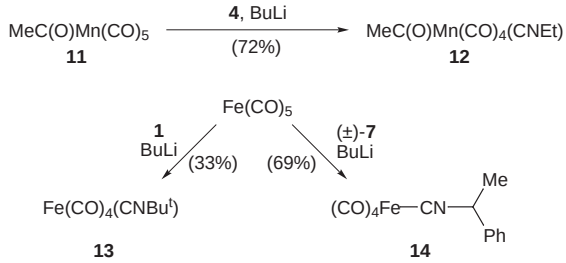
Phosphoramidate **1** was dissolved in THF, cooled to −78 °C and treated with 1 equiv. of butyllithium.¶ To this solution was added to a stirred suspension of 1 equiv. of cation **2** in THF. The resulting mixture was held at −78 °C for 6 h during which time the suspension gradually gave way to a yellow solution. Work-up of the product mixture by column chromatography and crystallisation produced a light yellow solid which was identified as the dicarbonyl isonitrile complex **3** by comparison of its ^{1}H NMR and IR spectra with literature values.[9] Cation **3** was generated in an acceptable 58% yield on a 1.0 mmol scale, thus indicating that the phosphoramidate-mediated conversion of carbonyl ligands to isonitrile ligands is indeed feasible.

Experiments to probe the scope and limitations of this process with respect to the phosphoramidate were performed next. Thus cation **2** was reacted with 2 equiv. of the ethylamine-derived phosphoramidate **4** and methyllithium. This experiment gave the diisonitrile product **5**[10] in 77% yield. Moreover reaction of cation **3** with 1 equiv. of phosphoramidate **4** and methyllithium gave the novel‖ cation **6** in 63% yield. These experiments demonstrate not only that the degree of carbonyl–isonitrile conversion can be controlled by the amount of phosphoramidate used and that the method is useful for the controlled formation of mixed isonitrile complexes, but also that complexes of volatile isonitriles are readily and conveniently formed by this approach.

In view of the rarity of non-racemic chiral isonitrile complexes, phosphoramidate (*S*)-**7** was synthesised from (*S*)-α-methylbenzylamine. Reaction of the anion of **7** with cation **2** smoothly generated the novel cation **8** in 55% yield. Thus the



Scheme 1



Scheme 2

method provides a straightforward and new way of incorporating chirality into transition metal complexes. Moreover, a wide variety of amines, which provide the chirality, is readily available.

Initial experiments on the scope and limitations of the conversion with respect to transition metal substrates have also been performed. Thus the triphenylphosphine-substituted iron cation **9** was synthesised according to a literature procedure[11] and reacted with the anion of phosphoramidate **4** to give the isonitrile **10**[12] in 47% yield. Likewise the manganese acetyl complex **11** was synthesised[13] and reacted with the anion derived from phosphoramidate **4** thus producing the novel manganese isonitrile complex **12** in 72% yield (Scheme 2), and iron pentacarbonyl was reacted with the anions of **1** and (±)-**7** to give isonitrile complex **13**[14] and the novel complex **14** respectively.

Finally, to check the stereochemical consequences of the metal isonitrile synthesis, iron pentacarbonyl was reacted with the anion of (*S*)-**7**. Chiral HPLC analysis of the products** from the reactions of iron pentacarbonyl with the anions of (±)-**7** and (*S*)-**7** revealed that the product derived from (*S*)-**7** was formed in 99 ± 1% ee, indicating that racemisation of the amine does not occur during its incorporation into the isonitrile ligand.

Notes and References

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‡ Phosphinimines, $Ph_3P{=}NR$, are known to convert metal carbonyl ligands into metal isonitrile ligands (ref. 5). In contrast to phosphoramidates, however, phosphinimines are frequently moisture and/or air-sensitivity (refs. 5, 6).

§ For example, a recent report on the enantioselective bis-silylation of alkenes using a palladium(0) chiral isonitrile catalyst (ref. 7), represents, to the best of our knowledge, the only use of chiral isonitriles in asymmetric catalysis to date.

¶ The method used for the conversion of cation **2** to cation **3** is in fact typical of the protocols used for all the other carbonyl–isonitrile conversions discussed herein. Thus, Bu^nLi (1.6 mol dm^{-3}; 0.63 cm^3, 1.0 mmol) was added dropwise to a solution of *N*-(*tert*-butyl)phosphoramidate **1** (0.209 g, 1.00 mmol) in THF (10 cm^3) held at −78 °C under nitrogen. The solution was allowed to warm to room temperature and then recooled to −78 °C for the addition, *via* a cannula and under nitrogen, of a suspension of cation **2** (0.350 g, 1.00 mmol) in THF (30 cm^3). The reaction mixture was stirred at −78 °C for 6 h. Solvent removal gave a brown solid which was subjected to column chromatography [SiO_2; light petroleum (bp 40–60 °C)–acetone, 1 : 1]. The resulting yellow solid was crystallised from acetone–CH_2Cl_2 to give cation **3** (0.235 g, 58%) as yellow crystals.

‖ The novel complexes **6**, **8**, **12** and **14** all gave satisfactory spectroscopic (IR, ^1H NMR, ^{13}C NMR and low resolution MS) and microanalytical or high resolution MS data.

** Chiralcel OD-H; Pr^iOH–hexane (1 : 40), 900 μl min^{-1}; retention times of enantiomers: 6.37 and 6.83 min.

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