Phosphoramidate mediated conversion of tricarbonyl(vinylketene)-iron(0) complexes into tricarbonyl(vinylketenimine)iron(0) complexes

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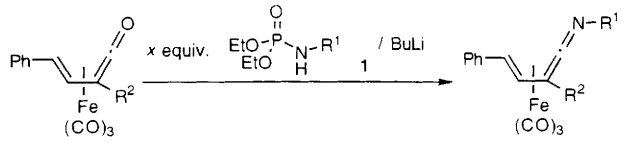
The anions of diethyl *N*-alkyl(aryl)phosphoramidates **1** react with tricarbonyl(vinylketene)iron(0) complexes **2** to give tricarbonyl(vinylketenimine)iron(0) complexes **3**; the yield of **3** is dependent on the steric bulk of the phosphoramidate substituent R^1 and the degree of substitution of the vinylketene complex substituent R^2.

Our recent interest in the chemistry of tricarbonyl(vinylketene)-iron(0) complexes has led us to investigate their reactivity towards alkynes,[1] alkenes,[2] nucleophiles,[3] phosphonoacetate anions[4] and isocyanides.[5] In the last-mentioned case, we found that isocyanides reacted with the vinylketene complexes at 80 °C in 10–24 h to produce tricarbonyliron(0) complexes of vinylketenimines. We are currently interested in probing the reactivity of the vinylketenimine complexes in more detail in order to compare and contrast it with the reactivity of the vinylketene complexes. Although the isocyanide route to tricarbonyl(vinylketenimine)iron(0) complexes from vinylketene complexes is viable, producing the required complexes in 51–71% yield,[5] it is limited by the volatility, the toxicity and the malodorous properties of some isocyanides. We therefore report herein a new method of converting tricarbonyl(vinylketene)iron(0) complexes into tricarbonyl(vinylketenimine)-iron(0) complexes. The method, which employs mild reaction conditions, broadens the range of substituents that can easily be placed on the nitrogen atom of the ketenimine complex, the electronic and steric properties of which may well play an important role in the reactivity of these species.

Diethyl *N*-alkyl(aryl)phosphoramidate anions $\mathbf{1}^-$ have been shown to react with an excess of phenylethylketene to give the corresponding ketenimines in 18–62% yield.[6] As diethyl *N*-alkyl(aryl)phosphoramidates are readily available from diethyl phosphite and primary amines,[7] it was postulated that the addition of their anions to tricarbonyl(vinylketene)iron(0) complexes should provide a convenient route to tricarbonyl-(vinylketenimine)iron(0) complexes. [Attempts to condense amines directly with tricarbonyl(vinylketene)iron(0) complexes under a range of conditions had proven unsuccessful.] Accordingly diethyl *N*-ethylphosphoramidate **1** (R^1 = Et) was prepared in 75% yield from diethyl phosphite and ethylamine following a literature procedure[7] and 1 equiv. of its anion, generated by treatment with butyllithium, was added to the vinylketene complex **2** (R^2 = Bu^t)[5b] at −78 °C in tetra-



2 **3**

hydrofuran (THF). After the reaction mixture had been allowed to warm to room temperature and stirred at that temperature for 14 h, analysis of an aliquot of the product mixture by ^{1}H NMR spectroscopy revealed that 80% of the vinylketene complex had been converted into a new complex. This was isolated by column chromatography and identified by its ^{1}H NMR, ^{13}C NMR, IR and mass spectra and its elemental analysis as the novel tricarbonyl(vinylketenimine)iron(0) complex **3** (R^1 = Et, R^2 = Bu^t).† The isolated yield of complex **3** (R^1 = Et, R^2 = Bu^t) was 50% (Table 1, entry 1). In order to optimise the yield of this reaction, it was repeated using 2.0 and 1.5 equiv. of diethyl *N*-ethylphosphoramidate (Table 1, entries 2 and 3). As these reactions both gave complete conversion and essentially the same high yield, 1.5 equiv. of the diethyl *N*-alkyl(aryl)phosphoramidate were used in subsequent reactions.

Table 1 Reaction of the anions of diethyl *N*-alkyl(aryl)phosphoramidates **1** with tricarbonyl(vinylketene)iron(0) complexes **2** to give tricarbonyl(vinylketenimine)iron(0) complexes **3**

Entry	R^1	R^2	x	Conversion (%)	Yield **3** (%)
1	Et	Bu^t	1.0	80	50
2	Et	Bu^t	2.0	100	90
3	Et	Bu^t	1.5	100	92
4	Et	Pr^i	1.5	100	78
5	Et	Me	1.5	100	41
6	c-C_6H_{11}	Pr^i	1.5	100	58
7	Bu^t	Pr^i	1.5	0	—
8	Ph	Pr^i	1.5	100	87

In order to define the scope and limitations of the reaction, the effect of varying the vinylketene complex substituent R^2 was examined. Thus, vinylketene complexes in which R^2 = Pr^i and R^2 = Me were treated with the anion of diethyl *N*-ethylphosphoramidate (Table 1, entries 4 and 5). These gave novel vinylketenimine complexes in 78 and 41% yield, respectively. It is evident that the yield of the vinylketenimine complex falls dramatically as the level of substitution of R^2 is reduced. This decrease in yield is tentatively attributed to a competing deprotonation of R^2 by the phosphoramidate anion.

The effect of varying the substituent R^1 on the phosphoramidate anion was also probed. Accordingly, the previously reported diethyl *N*-alkyl(aryl)phosphoramidates derived from cyclohexylamine,[7] *tert*-butylamine[6] and aniline[7] were prepared by the procedure used before[7] and their anions treated with vinylketene complex **2** (R^2 = Pr^i). The results obtained from

† All the tricarbonyl(vinylketenimine)iron(0) complexes **3** were found to be novel, and they all gave satisfactory IR, ^{1}H NMR, ^{13}C NMR, low resolution mass spectral and microanalytical/high resolution mass spectral data.

these experiments (Table 1, entries 6–8) reveal that the success or otherwise of the reaction is dependent on the steric demands of the nitrogen substituent. Thus, although the reaction becomes less efficient when the ethyl group is replaced by a cyclohexyl group and fails altogether with a *tert*-butyl group, it proceeds in high yield with the less sterically demanding phenyl-substituted phosphoramidate.

In summary, we have discovered and started to define the scope and limitations of a convenient and versatile route to tricarbonyliron(0) complexes of vinylketenimines. This should not only facilitate a study of the chemistry of these complexes, but it may also provide a route to enantiomerically pure vinylketene complexes. Preliminary experiments suggest that phosphoramidate anions derived from chiral amines react preferentially with one enantiomer of the vinylketene complexes.

Experimental

The following procedure for the conversion of diethyl *N*-phenylphosphoramidate **1** (R^1 = Ph) and vinylketene complex **2** (R^2 = Pr^i) into vinylketenimine complex **3** (R^1 = Ph, R^2 = Pr^i) is typical.

Butyllithium (1.55 mol dm^{-3}; 0.96 cm^3, 1.49 mmol) was added to a stirred solution of diethyl *N*-phenylphosphoramidate **1** (R^1 = Ph) (0.349 g, 1.52 mmol) in THF (10 cm^3) at −78 °C and the mixture stirred for 10 min. The resulting colourless solution was then allowed to warm to room temperature over a period of 30 min. After the mixture had been re-cooled to −78 °C, vinylketene complex **2** (R^2 = Pr^i) was added to it and the yellow solution was then slowly warmed to room temperature and stirred for 14 h. Column chromatography (SiO_2; dichloromethane) of the resultant brown solution readily gave an orange crystalline solid. Recrystallisation of this from dichloromethane–light petroleum (bp 40–60 °C) gave complex **3** (R^1 = Ph, R^2 = Pr^i) (0.347 g, 87%) as orange crystals, mp 63–64.5 °C (Found: C, 65.7; H, 4.8; N, 3.5. $C_{22}H_{19}FeNO_3$ requires C, 65.86; H, 4.77; N, 3.49%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2053vs, 1988vs br (C≡O) and 1713m br (C=N); δ_H(270 MHz; $CDCl_3$) 1.36 (3 H, d, *J* 7, CH_3CH), 1.43 (3 H, d, *J* 7, CH_3CH), 2.63 (1 H, sept, *J* 7, Me_2CH), 2.92 (1 H, d, *J* 9, PhC*H*), 6.12 (1 H, d, *J* 9, PhCH=C*H*), 7.0–7.1 (2 H, m, arom.), 7.2–7.35 (6 H, m, arom.) and 7.4–7.45 (2 H, m, arom.); δ_C(100.6 MHz; $CDCl_3$) 20.9 (CH_3), 21.8 (CH_3), 28.8 (*C*HMe_2) 59.4 (Ph*C*H), 71.9 (*C*Pr^i), 89.3 (PhCH=*C*H), 120.9, 124.8, 126.4, 127.1, 128.9, 129.0 (C_{ortho}, C_{meta} and C_{para}), 138.7 (CC_{ipso}), 151.1 (NC_{ipso}), 195.4 (C=*C*=N), 205.7br and 210.8br (C≡O); *m*/*z* (CI, NH_3) 402 (MH^+, 100%), 374 (14, MH − CO), 346 (2, MH − 2CO), 317 (15, M − 3CO) and 262 [59, MH − $Fe(CO)_3$].

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