Alkylation of Tricarbonyliron Complexes by Trimethylsilyl Cyanide: Synthetic and Kinetic Studies

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Trimethylsilyl cyanide has been shown to be a synthetically useful reagent for the alkylation of tricarbonyl(η^5-cyclohexadienyl)iron(1+) salts, particularly in cases where the reactive terminus of the dienyl system bears an alkyl substituent. The reaction proceeds *via* the isocyanide isomer, with a rate-limiting pre-equilibration of the reagent. In cases where reactive metal complexes were used, the rate of reaction was proportional to the concentration of Me_3SiCN, and was independent of both the nature and concentration of the dienyl salt. In the case of the deactivated 2-methoxy substituted dienyl salt, non-linear rate plots indicated a change in the rate-limiting step.

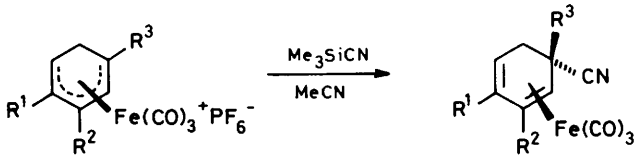
Tricarbonyliron complexes are notable for their ability[1] to react with a wide variety of nucleophiles to give stereocontrolled products in high yield. The versatility of these compounds as electrophiles has led to their application[2] as key intermediates in organic synthesis. Unfortunately, substitution by an alkyl group at a terminus of the dienyl system of complexes of type (**1**) (see Scheme 1) severely curtails the range of suitable nucleophiles, since in many cases competing deprotonation results[3] in the formation of triene complexes. We have recently reported an example[4] where the limitation by steric effects of reaction of complexes of type (**1**) with cyanide has been overcome by the use of the reagent trimethylsilyl cyanide.[5] We now describe the results of studies designed to explore the synthetic potential and mechanistic implications of this reaction.

Two factors are important when considering the differences in reactivity between the cyanide anion and trimethylsilyl cyanide. The ability to effect alkylation rather than deprotonation indicates that Me_3SiCN is a far less basic reagent, and that dissociation to form a free cyanide anion is not involved in its reaction with tricarbonyliron complexes. In order to provide information for the design of further reagents for use with hindered metal complexes we have sought to account for the non-basic character of Me_3SiCN. Difficulties with regiocontrol can also be a limitation in alkylation reactions of this type. The regiochemistry of alkylation reactions employing Me_3SiCN has been examined to explore the synthetic potential and chemical nature of the reactive species.

Results and Discussion

Synthetic Reactions.—An examination of the alkylation of a range of tricarbonyliron complexes by Me_3SiCN has confirmed the conclusion made from preliminary studies[4] that this compound is a versatile and high yielding reagent for this purpose (Scheme 1). The range of yields indicated in Table 1 show this to be a highly efficient synthetic reaction. Particularly in cases where a terminus of the dienyl system is blocked by a substituent, the reagent is the best currently available for this purpose. In contrast to the reaction with cyanide anion, however, a typical feature of these alkylations is that the reaction proceeds relatively slowly and requires a substantial excess of the reagent. The use of Me_3SiCN, rather than a simple inorganic cyanide, is thus most appropriate when the organometallic complex is of particular value and thus yield becomes the criterion of paramount importance.

Tetra-n-butylammonium cyanide was also evaluated. This reagent underwent a rapid reaction with complexes without substituents at the terminus of the dienyl system, but was unsatisfactory in other circumstances. The reagent has subsequently been used[6] to good effect in the alkylation of an $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]^+$ alkene complex.



(**1**) (**2**)

(**a**) $R^1 = R^2 = R^3 = H$
(**b**) $R^1 = R^3 = H$, $R^2 = OMe$
(**c**) $R^1 = R^3 = H$, $R^2 = Me$
(**d**) $R^1 = OMe$, $R^2 = R^3 = H$
(**e**) $R^1 = OMe$, $R^2 = H$, $R^3 = Me$

Scheme 1.

Kinetic Studies.—Measurement of the kinetics of the reaction between (**1**) and Me_3SiCN provides useful insight into the nature of the reaction, the requirement for a large excess of Me_3SiCN, and the non-basic character of the alkylating species. The protocol for this investigation was largely based on earlier studies of tricarbonyliron complexes by Kane-Maguire *et al.*,[7] in which the progress of the reaction was followed by i.r. spectroscopy. In our work, however, the carbonyl stretching frequency of the starting material (**1**) at 2 100 cm^{-1} overlapped with the nitrile stretching frequencies of the reagent at 2 180 (ν_{CN}) and 2 100 (ν_{NC}) cm^{-1} and the rate of appearance of the corresponding absorbance at 1 969 cm^{-1}, due to the diene product, (**2**), was measured instead. Concentrations of (**2**) were measured from the magnitude of the i.r. absorbance at 1 969 cm^{-1} by employing a calibration plot of concentration against absorbance, which was linear following Beer's law. Preliminary experiments indicated that the rate of reaction was dependent only on the concentration of Me_3SiCN. A zero-order rate expression thus defines $k_{obs.}$, equation (1).

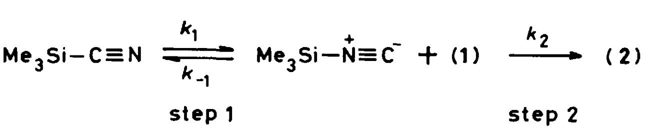
$$\frac{d[\text{product}]}{dt} = k_{obs.}[\text{dienyl complex}]^0 = k_1[\text{dienyl complex}]^0\,[Me_3SiCN] \qquad (1)$$

Accurate values for $k_{obs.}$, determined from a series of experiments in which the initial concentration of the dienyl complex was kept constant at 0.05 mol dm^{-3}, were obtained from plots

Table 1. Alkylation of tricarbonyliron complexes by cyanide reagents

Starting material	Product	Ratio	Reagent	Yield (%)	Ref.
(1a)	**(2a)**	—	Me_3SiCN	83	*a*
			NaCN	52	18
(1b)	**(2b)**	—	Me_3SiCN	88	*a*
			NaCN	74	19
(1d)	**(2d)**	—	Me_3SiCN	69	*a*
			NaCN	58	18
			NBu_4CN	75	*a*
(1e)	**(2e)**	—	Me_3SiCN	96	*a*
			NaCN	52	20
(4a)	**(5a)**, **(6a)**	2:1	Me_3SiCN	85	*a*
		2:1	NaCN	90^b	14
(4b)	**(5b)**, **(6b)**	1:2	Me_3SiCN	97	*a*

[a] This work. [b] Crude yield; products converted without isolation to acetyl derivatives.



$$Me_3Si{-}C{\equiv}N \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Me_3Si{-}\overset{+}{N}{\equiv}\overset{-}{C} + (1) \xrightarrow{k_2} (2)$$

step 1 step 2

Scheme 2.

of concentration *versus* time and are presented in Table 2. The results given in entries 5—7 indicate that salts which normally[8] display a range of rates in their reactions with nucleophiles react at the same rate, within experimental error, with Me_3SiCN, an observation which strongly suggests that the rate-limiting step in this reaction is prior to the involvement of the salt itself. Variation of the excess of Me_3SiCN (Table 2, entries 1, 2, 4, and 5) indicated that the rate of reaction was proportional to the concentration of the reagent. A value for k_1, of $(1.7 \pm 0.1) \times 10^{-5}\ s^{-1}$, was determined from a plot of $k_{obs.}$ against $[Me_3SiCN]$ (Table 2, entries 1—7) which was linear (correlation coefficient = 0.992) over the range of concentrations examined. The results obtained are consistent with a proposed slow pre-equilibrium of Me_3SiCN and Me_3SiNC followed by a rapid reaction of Me_3SiNC with the salt (Scheme 2). The general rate law for such a situation, applying the steady-state approximation,[9] is given in equation (2).

$$\frac{d[\text{product}]}{dt} = \frac{k_1k_2[\text{dienyl complex}]\,[Me_3SiCN]}{k_{-1} + k_2[\text{dienyl complex}]} \qquad (2)$$

In cases where the first step (Scheme 2) is rate limiting, k_2[dienyl complex] is much greater than k_{-1} and the rate expression then reduces to the form shown in equation (3).

$$\frac{d[\text{product}]}{dt} = k_1[Me_3SiCN] \qquad (3)$$

A contrast to these results was obtained when the 2-OMe substituted salt (**1d**) was employed. This complex is known[8] to be far less reactive than (**1a**)—(**1c**) and in this case the rate of reaction with Me_3SiCN was also reduced, suggesting that the initial step in Scheme 2 is no longer rate limiting. In this case the plot of concentration against time was non-linear, as would be expected from the rate equation (4) which is obtained by rearrangement of equation (2). If the value of the partition factor, k_{-1}/k_2[dienyl complex], is not negligible, as was assumed for the more reactive salts, then the rate has no simple dependence on the concentration of the salt. The increased involvement of the salt concentration in the rate expression [equation (2)] indicates a mechanistic changeover, from step 1 to step 2 (Scheme 2) being rate limiting.

$$\frac{d[\text{product}]}{dt} = \frac{k_1[Me_3SiCN]}{(k_{-1}/k_2[\text{dienyl complex}]) + 1} \qquad (4)$$

Table 2. Kinetic data for reaction of Me_3SiCN with tricarbonyl(cyclohexadienyl)iron(1+) complexes in MeCN; [Fe] = 0.05 mol dm^{-3}

Entry	Dienyl salt	$[Me_3SiCN]$/ mol dm^{-3}	$10^6\ k_{obs.}{}^a$/mol dm^{-3} s^{-1}		$k_{rel}{}^b$ (ref. 8)
1	**(1a)**	0.227	$3.0 \pm 0.1^c\ (0.998)^d$		—
2		0.455	6.2 ± 0.3 (0.995)		—
3		0.545	9.0 ± 0.6 (0.983)		—
4		0.545	9.1 ± 0.2 (0.998)		—
5		0.909	14.3 ± 0.3 (0.999)	14.5 ± 0.7	1.00
6	**(1b)**	0.909	15.2 ± 0.7 (0.996)		1.40
7	**(1c)**	0.909	14.1 ± 0.6 (0.997)		0.81
8	**(1d)**	0.909	*e*		0.09

[a] Determined at 25 °C. [b] Determined at 40 °C. [c] The uncertainties quoted are the standard deviations. [d] Correlation coefficients are given in parentheses. [e] Non-linear rate plot.

The interconversion of Me_3SiCN and Me_3SiNC has been a subject of considerable investigation.[10] In an ^1H n.m.r. study at 40 MHz, the observation of a single resonance from a sample known from its i.r. spectrum to comprise a mixture of Me_3SiCN and Me_3SiNC was interpreted[10] to support the operation of a labile equilibrium between the two compounds. Indeed other experiments confirmed that scrambling of isotopic labels was occurring on the n.m.r. time-scale. The authors concluded[10] that either a labile equilibrium between Me_3SiCN and Me_3SiNC, or a rapid exchange of CN groups between Me_3SiCN molecules alone, could account for the results. Earlier i.r. experiments,[11] however, have confirmed the equilibration of Me_3SiCN and Me_3SiNC, by observation of small changes in the relative intensities of i.r. absorbances at different temperatures, but give no indication of the time taken for such changes to occur. Our work indicates that the interconversion of Me_3SiCN and Me_3SiNC must occur relatively slowly. A rapid exchange of CN between molecules of Me_3SiCN, which would not affect our kinetic results, may account for the results obtained in the n.m.r. investigation.

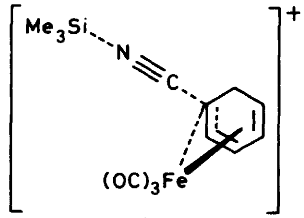
While there are many examples of reactions in which a pre-equilibrium step is rate limiting, a particularly good case being the nitration of aromatic substrates,[12] previous studies of the reaction of nucleophiles with tricarbonyliron complexes have indicated either a rapid pre-equilibrium of the nucleophile to form a reactive species or direct addition of the reagent. When the pre-equilibrium is the rate-limiting step, information about the rate of reaction of the dienyl cation (k_2) is not directly available from the kinetic results. To make a comparison between the rate of addition of Me_3SiNC to (**1**) with rates obtained for other nucleophiles, a value for the equilibrium constant is required for the interconversion of (**1**) and Me_3SiNC. While the equilibrium constant (*K*) has not been measured in acetonitrile, a value of *K* in 1-chloronaphthalene is available[13] and this value can be taken as a lower limit for *K* in acetonitrile, since the extent of isomerisation to Me_3SiNC will be increased by increasing the polarity of the solvent. A higher limit for k_{-1} of $\sim 10^{-2}\ s^{-1}$ can be estimated by combining this value for *K* with the value for k_1 of $1.7 \times 10^{-5}\ s^{-1}$ determined above.

For the partition factor, k_{-1}/k_2[dienyl complex], to have any significant effect on the rate of the reaction, it must have a value of at least 0.1. This leads to a higher limit of k_2 for the 2-OMe

Table 3. Comparison of nucleophile reactivities

Dienyl complex	Nucleophile	k_2/ dm^3 mol^{-1} s^{-1}	Ref.
(**1a**)	Acetylacetonate	~100	*a*
(**1a**)	$P(OBu)_3$	135	7
(**1d**)	$P(OBu)_3$	24	7
(**1a**)	Me_3SiNC	<22[b]	*c*
(**1d**)	Me_3SiNC	<2[b]	*c*
(**1a**)	$P(OPh)_3$	0.035	7
(**1d**)	$P(OPh)_3$	0.0036	7

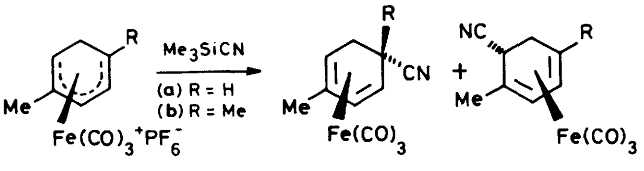
[a] L. A. P. Kane-Maguire, *J. Chem. Soc. A*, 1971, 1602. [b] Estimated values. [c] This work.



(**3**)

dienyl salt (**1d**) of 2 dm^3 mol^{-1} s^{-1}. By making use of the known[8] relative reactivity of complexes (**1a**) and (**1d**) (Table 2, entries 5 and 8), a corresponding value of 22 dm^3 mol^{-1} was obtained for the unsubstituted dienyl complex (**1a**). This indicates a relatively slow rate of nucleophile addition (see Table 3), which is consistent with the involvement of the zwitterionic isocyanide isomer rather than a fully charged anionic nucleophile.

Regiocontrol Studies.—The results of regiochemical investigations of these alkylation reactions are also consistent with the mechanistic view outlined above and the involvement of the transition state structure (**3**) in which carbon–carbon bond formation is accompanied by silicon–nitrogen bond breaking. In terms of regiocontrol, the reaction resembles the reaction with cyanide anion itself, since the bulk of the trimethylsilyl group is not well placed to interact with substituents on the dienyl ring system. Alkylation of the 2-methyl substituted salt (**4a**) with Me_3SiCN was in agreement with this conclusion (see below). The ratios of products (2:1) obtained were similar to ratios observed[14] for cyanide itself. Variation of the temperature of reaction had no significant effect on the product ratio. At low temperature (−20 °C), however, the rate of reaction became so slow that alkylation failed. The insensitivity of the ratio of products to changes in temperature contrasts with results obtained from studies involving other nucleophiles. Organocadmium reagents,[15] for example, show improved regioselectivity at low temperature while in the case of many anionic hydride reagents, regioselectivity worsens[14] as the temperature is reduced.



(**4**) (**5**) (**6**)

In order to examine further the effect of terminal methyl groups on alkylations involving Me_3SiCN, reaction with the 2,5-dimethyl substituted salt (**4b**) was examined. In this case predominant reaction was displaced to C^1, indicating that, despite the efficiency of alkylation at hindered sites when controlled by a strong directing group, the 5-methyl group in (**4b**) exerts a significant blocking effect.

Conclusions

Trimethylsilyl cyanide offers a suitable reagent for the alkylation of substituted positions on tricarbonyl(cyclohexadienyl)iron(1+) salts in cases where the reaction is controlled by a strong directing group. The results obtained are consistent with a view that the reaction proceeds *via* initial pre-equilibration to form the trimethylsilyl isocyanide isomer which then undergoes nucleophilic addition to the dienyl cation with loss of the silyl group. For all but the most unreactive dienyl cation complexes, the initial pre-equilibration step is rate determining. The synthetic value of this reaction could be improved if the excess of reagent required to effect conversion in a reasonable period of time could be reduced; attempts to catalyse the pre-equilibrium, and so increase the overall rate of the reaction in most cases, by use of $F_3CSO_3SiMe_3$, however, were unsuccessful. Nonetheless, the use of Me_3SiCN in place of a simple cyanide anion resulted generally in higher yields and provided vastly superior performance in cases where deprotonation can offer a competing reaction path. In contrast to the reactions of *O*-silylated enols[16] and allylsilanes[17] with cationic tricarbonyliron complexes, the reaction of Me_3SiCN proceeds *via* an intermediate in which the formation of a silicon–heteroatom bond involves extreme polarization of the molecule towards a zwitteronic structure. The reagent is thus highly nucleophilic, while showing very low basicity and lower susceptibility to steric hindrance.

Experimental

Trimethylsilyl cyanide[5] and the organo-iron complexes[1] were prepared and purified using published methods. Acetonitrile was distilled from calcium hydride under nitrogen and stored over calcium hydride. Synthetic reactions and kinetic experiments were performed under a nitrogen atmosphere. Product ratios were estimated from proton n.m.r. spectra recorded using a Perkin-Elmer EM-360 spectrometer. I.r. spectra were measured with a Perkin-Elmer 257 spectrometer using matched 0.1-mm calcium fluoride solution cells. When either KBr or NaCl solution cells were used, spurious results were obtained, due to competing reactions of the dienyl complexes with the halide windows.

Synthetic and Regiocontrol Studies.—*General procedure for addition of cyanide using trimethylsilyl cyanide.* Trimethylsilyl cyanide (5 mmol) was added to a stirred solution of the tricarbonyl(η^5-cyclohexadienyl)iron(1+) hexafluorophosphate salt (1 mmol) in acetonitrile at room temperature [in the case of (**1a**), (**4a**), and (**4b**)] or under reflux [in the case of (**1b**)—(**1e**)]. The reaction was followed by i.r. spectroscopy. After 3—4 h, the reaction mixture was allowed to cool to room temperature, and poured into water (50 cm^3). The product was extracted twice with diethyl ether (50 cm^3) and the combined extracts dried over magnesium sulphate. The solvent was removed by evaporation *in vacuo*, to give the crude product. The product was purified by radial chromatography, using diethyl ether–light petroleum (1:10) as eluant.

The following complexes were obtained in this way: tricarbonyl(η^4-5-*exo*-cyanocyclohexa-1,3-diene)iron(0)[18] (**2a**), 83%; tricarbonyl(η^4-5-*exo*-cyano-3-methoxycyclohexa-1,3-diene)iron(0)[19] (**2b**), 88%; tricarbonyl(η^4-5-*exo*-cyano-2-methoxycyclohexa-1,3-diene)iron(0)[18] (**2d**), 69%; tricarbonyl(η^4-5-*exo*-cyano-2-methoxy-5-*endo*-methylcyclohexa-1,3-diene)iron(0)[20] (**2e**), 96%; tricarbonyl(η^4-5-*exo*-cyano-2-methylcyclohexa-1,3-diene)iron(0) (**5a**) and tricarbonyl(η^4-6-*exo*-cyano-1-methylcyclohexa-1,3-diene)iron(0) (**6a**) as a 2:1 mixture of regioisomers,[14] 85%; tricarbonyl(η^4-5-*exo*-cyano-2,5-*endo*-dimethylcyclohexa-1,3-diene)iron(0) (**5b**) and tricarbonyl(η^4-6-*exo*-cyano-1,4-dimethylcyclohexa-1,3-diene)iron(0) (**6b**) as a 1:2 mixture of regioisomers, 97% (Found: C, 52.95; H, 4.10; N, 5.10. $C_{12}H_{11}FeNO_3$ requires C, 52.80; H, 4.05; N, 5.15%); $\nu_{max.}$(CO) at 2 047, 1 972 cm^{-1} (cyclohexane); δ_H ($CHCl_3$) 5.38 (d, 7 Hz), 5.15 (m), 3.20 (m), 3.05 (d, 5 Hz), 3.0—1.4 (m), 2.14 (s), 1.66 (s), 1.60 (s), and 1.37 (s) p.p.m. [the isomer ratio was estimated from the intensities of signals at 1.66 and 1.60 p.p.m. (major product) and at 2.14 (2-Me) and 1.37 p.p.m. (1-Me) (minor product)]; *m/z* 273 (M^+), 245, 217, 189, 187, 173, 163.

The formation of (**5a**) and (**6a**) was also examined at 40 °C and at -20 °C. At 40 °C a virtually identical ratio of products was obtained. At -20 °C the reaction proceeded too slowly to be of use.

Reaction of Tetra-n-butylammonium Cyanide with Tricarbonyl(η^5-2-methoxycyclohexadienyl)iron(1+), (**1d**).—A solution of tetra-n-butylammonium cyanide (0.295 g, 1.1 mmol) in acetonitrile (1 cm^3) was added dropwise to a stirred solution of (**1d**) (0.395 g, 1 mmol) in acetonitrile (2 cm^3) at 0 °C. The reaction mixture was stirred for 15 min at 0 °C, and then allowed to warm to room temperature. Methyl iodide was added (to destroy excess tetra-n-butylammonium cyanide) and the reaction mixture was poured into water (10 cm^3) and the product extracted with Et_2O (10 cm^3). The organic layer was washed with brine (10 cm^3) and dried ($MgSO_4$). Removal of the solvent by evaporation *in vacuo* gave the crude product. Purification by radial chromatography [Chromataton, 2-mm plate, diethyl ether–light petroleum (1:10) eluant] gave the pure product (**2d**) (0.207 g, 75%) (R_f 0.13).

Kinetic Studies.—A 5 × 10^{-2} mol dm^{-3} acetonitrile solution (10 cm^3) of the tricarbonyl(cyclohexadienyl)iron(1+) salt was placed in a 25-cm^3 flask and stirred while maintained at 25 °C (±0.1 °C) in a thermostatted bath. Trimethylsilyl cyanide was added by syringe to produce the required concentration of the reagent ([Me_3SiCN] = 0.227, 0.455, 0.545, or 0.909 mol dm^{-3}). Samples were withdrawn by syringe (0.1 or 0.04 cm^3) at periodic intervals and diluted with acetonitrile (0.5 or 0.1 cm^3 respectively). For the reactions [Me_3SiCN] = 0.909 mol dm^{-3}, the interval between sampling was too short to allow immediate measurement of the i.r. spectrum. In this case the samples were initially sealed in plastic vials and stored in liquid nitrogen. Spectra were measured when the kinetic run had been completed. The i.r. spectra of the samples were recorded over the region 2 180—1 900 cm^{-1}, comprising the carbonyl peaks at 2 110 and 2 060 cm^{-1} due to the starting materials and the growing bands at *ca.* 2 020 and 1 970 cm^{-1} associated with the diene product. The reactions were studied by following the increase of the lowest wavelength carbonyl band of the product (*e.g.* 1 969 cm^{-1}); zero-order rate constants (Table 2) were obtained from the slopes of plots of area under absorbance *versus* time. Linear kinetics were generally observed for 10—80% of the reaction.

Calibration.—Tricarbonyl(η^4-5-cyanocyclohexa-1,3-diene)iron(0) (68.8 mg, 0.28 mmol) was dissolved in acetonitrile (100 cm^3). 1, 2, 3, 4, 5, 6, 7, and 8 cm^3 aliquots were made up to 10 cm^3 of acetonitrile and the i.r. spectra over the region 2 180—1 900 cm^{-1} recorded for the original solution and these solutions. A linear plot of absorbance against concentration with a correlation coefficient of 0.998 was obtained. Calibration points for other complexes were found to lie on the same line within experimental error.

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