Preparation of Tricarbonyl(η^6-pyridine)chromium(0) Complexes

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The synthesis of tricarbonyl(η^6-pyridine)chromium(0) complexes is accomplished *via* complexation of 2-silylpyridines with subsequent fluoride ion-mediated desilylation under mild conditions. The tricarbonylchromium(0) complexes of pyridine, 2-methylpyridine, 3-methylpyridine, 2-ethylpyridine, 2-(but-3-enyl)pyridine and 2-(6-trimethylsilylpyridyl)-1,3-dioxolane are prepared. Deprotonation (lithium diisopropylamide) and methylation (methyl iodide) of tricarbonyl(η^6-pyridine)chromium(0) converts it cleanly into tricarbonyl(η^6-2-methylpyridine)chromium(0).

Thermolysis of hexacarbonylchromium with pyridine generates tricarbonyl trispyridinechromium, the pyridines being co-ordinated through their nitrogen lone pairs.[1] Thus, the preparation of η^6-pyridine complexes by a direct thermolysis method is precluded. However, the preparations of a small number of tricarbonyl(η^6-pyridine)chromium(0) complexes are known but all the complexes so far described, with one exception,[2] have bulky alkyl groups at the 2- and 6- positions to suppress coordination of the lone pair.[3] This is a serious drawback in the subsequent chemical elaboration of these complexes as most of the interesting chemistry of uncomplexed pyridine derivatives and therefore presumably of their complexes occurs at the 2-position.[4]

We now report the first general method for the preparation of tricarbonyl(η^6-pyridine) chromium(0) complexes with vacant 2- and 6-positions *via* complexation of hindered 2-silylpyridines, the silyl group providing steric protection for the nitrogen lone pair, with subsequent removal of the protecting group. Part of this work has been previously communicated.[5]

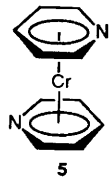
Results and Discussion

The precursor to the parent complex tricarbonyl(η^6-pyridine)chromium(0) **1** was selected as tricarbonyl[η^6-bis(trimethylsilyl)pyridine]chromium(0) **2**. The known 2,6-bis(trimethylsilyl)pyridine **3** was prepared by the literature procedure in good yield[6] from commercially available 2,6-dibromopyridine **4**. The ^{1}H NMR spectrum of compound **3** showed an 18 H singlet at δ 0.33 as well as a 3 H multiplet around δ 7.40. Treatment of **3** with hexacarbonylchromium in refluxing dioxane for 30 h resulted in a dark yellow–green solution which was filtered through alumina to leave an orange oil upon evaporation of solvent. Flash chromatography, eluting with light petroleum–ether (15:1) gave, after removal of solvent, an amber-coloured crystalline solid. An upfield shift of the pyridine hydrogen peaks by *ca.* 2 ppm at δ 5.48 (d) and 5.29 (s) together with the singlet at 0.33 (ratio 2:1:18) in the ^{1}H NMR spectrum suggested the formation of complex **2** since upfield shifts of aryl protons are characteristic of η^6-coordination of arenes. IR data, a molecular ion *m/z* 360 ($M^+ + 1$) and an elemental analysis confirmed this assignment.

Treatment of a THF solution of **2** with tetrabutylammonium fluoride trihydrate and then quenching with water failed to induce desilylation. However, addition of water with the tetrabutylammonium fluoride trihydrate at −78 °C and stirring the solution at room temperature in the dark for 1.5 h led, after evaporation of solvent and flash chromatography (eluting with ether), to tricarbonyl(η^6-pyridine)chromium(0) **1** (86%) as a light and air-sensitive yellow crystalline solid which could be recrystallised from isopentane and stored in the dark at −20 °C under an inert atmosphere.

The yellow colour was indicative of a tricarbonylchromium(0) complex, the upfield shift of the three sets of signals at δ 6.56, 5.65 and 5.26 showed the expected characteristic shift of the coordinated pyridine relative to the free ligand, which has peaks at δ 8–7. Absorbances in the IR spectrum at 1985 and 1920 cm^{-1} confirmed the presence of the tricarbonylchromium(0) unit and a molecular ion *m/z* at 215 were all consistent with a 1:1 complex between pyridine and tricarbonylchromium(0). A satisfactory elemental analysis confirmed the π-coordination of the tricarbonylchromium(0) moiety in **1**.

The above reactions demonstrate that two trimethylsilyl groups provide ample steric hindrance of the nitrogen lone pair thus eliminating the possibility of σ-coordination. It was of interest to see how much steric bulk was required to promote π-complexation and whether mono-silylated pyridines could be used. One other example of this type of protection utilising two silyl groups has been recently reported independently in the synthesis of sandwich complex bis(pyridine)chromium **5**.[7]



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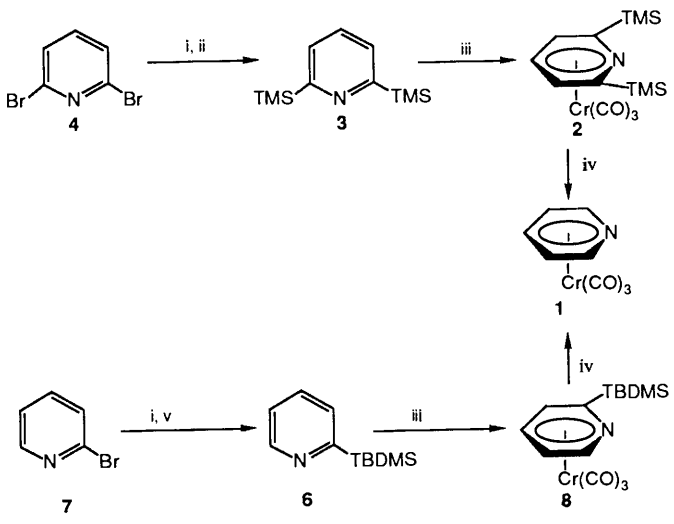
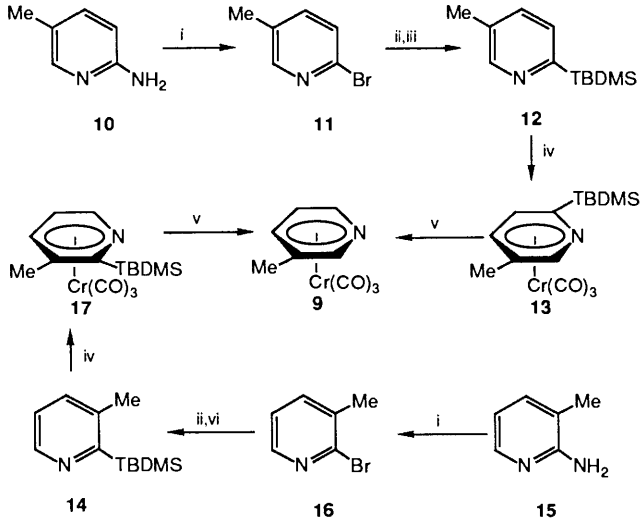
The novel 2-t-butyldimethylsilylpyridine **6** was prepared by quenching 2-pyridyllithium, derived from 2-bromopyridine **7**, with t-butyldimethylsilyl chloride and fully characterised. The ^{1}H NMR spectrum of **6** includes a 6 H singlet at δ 0.35 corresponding to the two equivalent silyl methyl groups. Thermolysis of hexacarbonylchromium with **6** under the standard conditions gave a yellow crystalline product (20%) assigned as tricarbonyl(η^6-2-t-butyldimethylsilylpyridine)chromium(0) **8**. This exhibited ^{1}H NMR peaks corresponding to four complexed arene protons, a 9 H singlet at δ 0.92 and two 3 H singlets at δ 0.38 and 0.32. Since the two faces of pyridine **6** are enantiotopic, complexation affords a racemic mixture of complex **8**, in which the two methyl groups of the t-butyldimethylsilyl group are diastereotopic; hence their distinct resonances. Complex **8** was fully characterised, including elemental analysis. Treatment of **8** with tetrabutylammonium fluoride trihydrate in wet THF as in the above case gave, upon work-up, a single yellow complex in essentially quantitative yield identical in all respects to the authentic sample of tricarbonyl(η^6-pyridine)-chromium(0) **1**, prepared earlier (Scheme 1).



Scheme 1 *Reagents:* i, BuLi, −78 °C; ii, TMSCl; iii, $Cr(CO)_6$, dioxane, reflux; iv, TBAF, H_2O; v, TBDMSCl

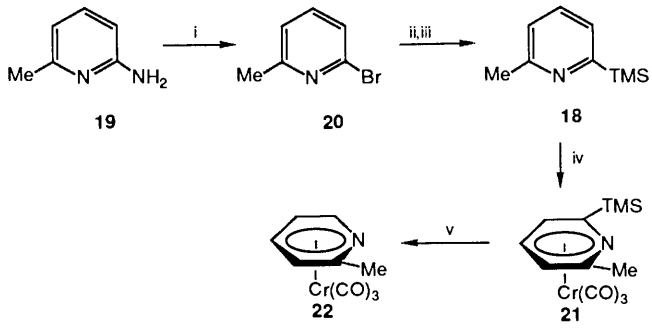
The formation of the monosilylated complex **8** and the facility of desilylation prompted the synthesis of tricarbonyl(η^6-3-methylpyridine)chromium(0) **9**. Two approaches to this complex were investigated. The bromo compound **11**, prepared *via* diazotisation of **10**,[8] was treated with butyllithium to generate the pyridyllithium species, which on quenching with t-butyldimethylsilyl chloride yielded the novel silylpyridine **12** (87%), as a crystalline solid which was fully characterised, including elemental analysis. Thermolysis of hexacarbonylchromium in the presence of **12** under the standard conditions (19 h) gave (η^6-2-t-butyldimethylsilyl-5-methylpyridine)tricarbonylchromium(0) **13** in modest yield (29%) as a yellow crystalline solid. The ^{1}H NMR spectrum of this complex contained two distinct 3 H singlet resonances at δ 0.37 and 0.30, consistent with the diastereotopic nature of the two methyls of the t-butyldimethylsilyl group which results on complexation of this prochiral pyridine. Desilylation of this compound with wet tetrabutylammonium fluoride trihydrate, followed by flash chromatography eluting with ether, gave tricarbonyl(η^6-3-methylpyridine)chromium(0) **9** as a highly crystalline light-sensitive solid (83%). The ^{1}H NMR spectrum of this complex exhibited a doublet at δ 6.47 (*J* 1.2 Hz) and a doublet of doublets at 6.43 (*J* 1.2 and 4.0 Hz), characteristic of the 2- and 6-protons, with long-range coupling between them. Other resonances at δ 5.54 and 5.29 along with a 3 H singlet at δ 2.19 reaffirmed this assignment. Tricarbonyl(η^6-3-methylpyridine)chromium(0) **9** together with its precursor complex **13** were fully characterised including satisfactory elemental analyses.

The second route to tricarbonyl(η^6-3-methylpyridine)-chromium(0) **9** was to synthesise the 2-t-butyldimethylsilyl-3-methylpyridine **14** from **15**[8] *via* **16**. Lithiation of **16** with butyllithium, but this time quenching with the more powerful electrophile t-butyldimethylsilyl triflate, gave a pure sample of **14**. That treatment with t-butyldimethylsilyl chloride failed to give satisfactory results was ascribed to the hindered nature of the lithiated species, and the poorer electrophilicity of this latter silylating reagent. Thermolysis of hexacarbonylchromium in the presence of **14** afforded (η^6-2-t-butyldimethylsilyl-5-methylpyridine)tricarbonylchromium(0) **17** (28%) as a crystalline solid. The ^{1}H NMR spectrum of complex **17** exhibited three contiguous protons in the range δ 5.50–5.00, a 3 H singlet at δ 2.22, 9 H singlet at 0.94 and two methyl resonances at δ 0.55 and 0.31. Full characterisation of this and the novel pyridine **14** confirmed their structures. Treatment of **17**, with tetrabutylammonium fluoride trihydrate as before gave tricarbonyl(3-methylpyridine)chromium(0) **9**, identical in every respect to the authentic sample previously prepared (Scheme 2).



Scheme 2 *Reagents:* i, HBr, Br_2, $NaNO_2$, 0 °C; ii, BuLi, −78 °C; iii, TBDMSCl; iv, $Cr(CO)_6$, dioxane, reflux; v, TBAF, H_2O; vi, TBDMSOTf

A single t-butyldimethylsilyl group attached to the 2-position of the pyridine ring having been shown to provide enough steric hindrance to promote π-complexation, it was now of interest to investigate the synthesis of tricarbonyl(η^6-pyridine)-chromium(0) complexes with a single alkyl group attached to the ring at the 2-position. The known 6-methyl-2-trimethylsilylpyridine **18** was synthesised from 2-amino-6-methylpyridine **19** in two steps. Treatment with bromine in the presence of nitrous acid gave the bromopyridine **20**[8] and subsequent lithiation followed by trimethylsilyl chloride quenching afforded **18**.[9] Thermolysis of hexacarbonylchromium in the presence of **18** under the standard conditions afforded, on work-up including flash chromatography, eluting with light petroleum–ether (5:1), the corresponding tricarbonylchromium(0) complex **21** (42%). The presence of three protons in the ^{1}H NMR spectrum in the range δ 6–5, a 3 H singlet at δ 2.41 and a 9 H singlet at δ 0.35 confirmed the π-coordination of the pyridine in the complex. Complex **21** was fully characterised including elemental analysis (Scheme 3).

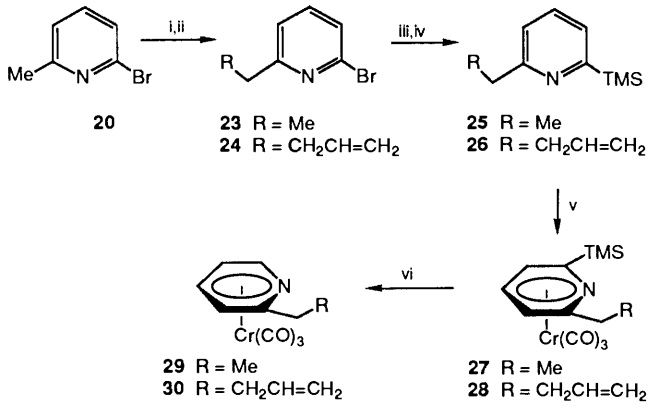


Scheme 3 *Reagents:* i, HBr, Br_2, $NaNO_2$, 0 °C; ii, BuLi, −78 °C; iii, TMSCl; iv, $Cr(CO)_6$, dioxane, reflux; v, TBAF, H_2O

Treatment of **21** with wet tetrabutylammonium fluoride trihydrate gave clean desilylation to afford tricarbonyl(η^6-2-methylpyridine)chromium(0) **22** as a yellow solid, in excellent (94%) yield on flash chromatographic work-up eluting with light petroleum–ether (1:4); identified by loss of the trimethylsilyl peak in the ^{1}H NMR spectrum and the appearance of one extra arene proton peak. The identity of this previously

reported,[2] but poorly characterised, complex was confirmed by mass spectrometry and an elemental analysis.

With this latter complex in hand it was now feasible to prepare other tricarbonyl(η^6-2-alkylpyridine)chromium(0) complexes. Since the acidity of methyl protons of picolines is well known, it was envisaged that other silylated pyridines could be prepared by deprotonation/alkylation reactions. Starting from 2-bromo-6-methylpyridine **20**, the novel 2-bromo-6-ethylpyridine **23** and 2-bromo-6-(but-3-enyl)pyridine (**24**) could be prepared by deprotonation (lithium diisopropylamide) of the methyl group of **20** and quenching with methyl iodide or allyl bromide. In turn, following the previous methodology, **23** and **24** were treated with butyllithium and quenched with trimethylsilyl chloride to afford the novel 2-trimethylsilyl-6-ethylpyridine **25** and 6-(but-3-enyl)-2-trimethylsilylpyridine **26** in good yield. All these new compounds were fully characterised, including elemental analysis. Both of the silylpyridines **25** and **26** were complexed to give the corresponding tricarbonylchromium complexes in the normal way. Tricarbonyl(η^6-6-ethyl-2-trimethylsilylpyridine)chromium(0) **27** was obtained as a yellow oil and had a ^{1}H NMR spectrum similar to that of **21**, except that the methyl group had been replaced by a methyl triplet and a 2 H multiplet due to the diastereotopic methylene protons. [6-(But-3-enyl)-2-trimethylsilylpyridine]tricarbonylchromium(0) **28** was also obtained as an oil, and showed similar peak patterns in the ^{1}H NMR spectrum. Both complexes were found to be light stable at normal temperatures, but decomposed on exposure to air. However, correct analytical data confirmed their purity. Complexes **27** and **28** were subjected to tetrabutylammonium fluoride trihydrate as before to afford the deprotected complexes tricarbonyl(η^6-2-ethylpyridine)chromium(0) **29** and [2-(but-3-enyl)pyridine]tricarbonylchromium(0) **30** in excellent yield (Scheme 4). Complex **29** was



Scheme 4 *Reagents:* i, LDA, −78 °C; ii, RX; iii, BuLi, −78 °C; iv, TMSCl; v, $Cr(CO)_6$, dioxane, reflux; vi, TBAF, H_2O

obtained as a yellow crystalline solid, whilst **30** was an oil, both being slightly light sensitive. Their identity was confirmed by full characterisation.

Addition of a THF solution of **1** to lithium diisopropylamide at −40 °C with stirring resulted in the initial yellow solution becoming somewhat orange; subsequent addition (−40 °C) of methyl iodide resulted in a yellowish brown solution. Work-up and flash chromatography, eluting with ether, allowed the isolation of a single yellow crystalline product whose ^{1}H NMR spectrum showed it to be tricarbonyl(η^6-2-methylpyridine)chromium(0) **22**, identical with the previously prepared authentic sample. This would have arisen by deprotonation at the 2-position to give the pyridyl complexed anion **31** with subsequent trapping by methyl iodide to afford **22** on work-up.

Complexation of arenes to tricarbonylchromium(0) is well known[10] to increase the acidity of aryl protons and hence the success of the deprotonation/alkylation sequence is not surprising. That the only product formed was that elaborated at the 2-position, is at first sight surprising since although the anion **31** would be thought to be inductively stabilised by the electronegative nitrogen atom, it would also be subject to severe mutual lone pair repulsions, this being very much the case for free pyridine.[11] Also the predicted stabilities of the three possible pyridyl anions derived from free pyridine is 3- > 4- > 2- on molecular orbital grounds.[12] Other results suggest that when the nitrogen lone pair becomes involved in bonding by quaternisation or formation of *N*-oxide derivatives, then deprotonation of the 2-position does become favourable.[13] That the deprotonation of complex **1** did not produce an intensely coloured solution, which is characteristic of radical anions, lends support to the argument that the $Cr(CO)_3$ moiety is stabilising the anion **31**. Coordination of the lithium cation to the nitrogen lone pair of **1** could increase the acidity of the 2-position and suppress the lone pair repulsions, this would in turn deliver the base to the 2-proton facilitating its removal as in Fig. 1.

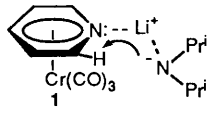
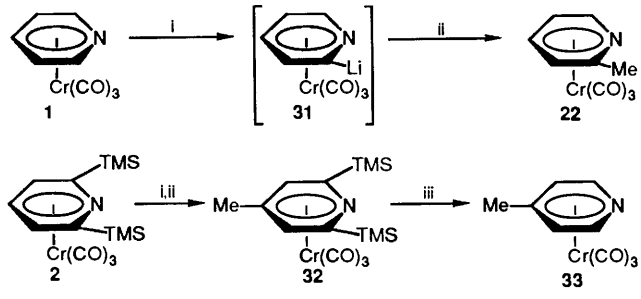


Fig. 1 Deprotonation of complex **1**

The next point to investigate was the outcome of the deprotonation reaction when both 2- and 6-positions were blocked. Treatment of bis-silylated complex **2** with lithium diisopropylamide under the same conditions as the previous case again gave an orange solution, which after quenching with methyl iodide afforded on work-up a single yellow product. The ^{1}H NMR spectrum of this material showed the presence of three singlets at δ 5.28, 2.09 and 0.33 with relative intensity ratio 2:3:18 showed that this was the 4-methylated complex **32**. A molecular ion *m/z* 373 and a correct elemental analysis confirmed this assignment. The formation of **32** is expected here on steric grounds since the very bulky trimethylsilyl groups prevent approach of the lithium diisopropylamide to the 3,5-protons and so only the 4-proton is available for deprotonation. Desilylation of complex **32** was achieved by treatment with wet tetrabutylammonium fluoride trihydrate as before under standard conditions to afford tricarbonyl(η^6-4-methylpyridine)chromium(0) **33** (76%) as a yellow microcrystalline solid. Complex **33** exhibited 2 H doublet peaks at δ 6.58 and 5.15 along with a methyl singlet peak at δ 2.21, consistent with the symmetrical nature of **33**. This compound was fully characterised, including elemental analysis (Scheme 5).

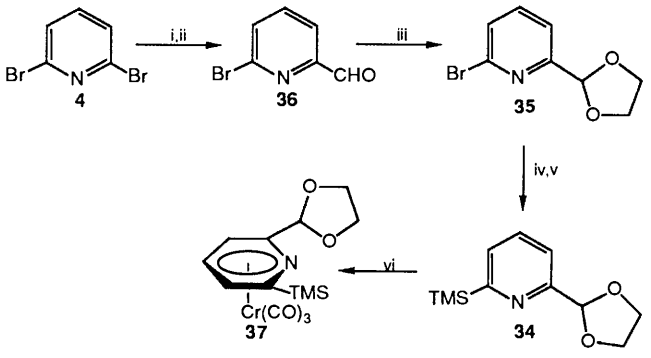


Scheme 5 *Reagents:* i, LDA, −40 °C; ii, MeI; iii, TBAF, H_2O

(η^6-Benzaldehyde)tricarbonylchromium(0) complexes cannot be prepared by direct complexation due to the electron withdrawing nature of the aldehyde group and its decarbonylation during complexation reactions.[14] Hence, attempted synthesis of a pyridine complex *via* complexation of a pyridinecarbaldehyde containing a free aldehyde group was rejected out

of hand. From the foregoing reactions it was necessary to synthesis a pyridine with both protection of the nitrogen lone pair and the aldehyde functionality. To this end the novel pyridine **34** was selected. The known 2-(2-bromo-6-pyridyl)-1,3-dioxolane **35** was synthesised from the aldehyde **36** prepared from 2,6-dibromopyridine **4** according to the literature procedure.[15] Careful lithiation of the acetal **35** at low temperature, followed by treatment of the resultant anion with trimethylsilyl chloride afforded on work-up with distillation 2-(2-trimethylsilyl-6-pyridyl)-1,3-dioxolane **34** as a colourless oil (73%). ^{1}H NMR analysis of this revealed three protons in the range δ 7.62–7.41, a singlet at δ 5.88 due to the acetal proton, a 4 H multiplet at δ 4.10 assigned as the methylene groups and a 9 H singlet at δ 0.32 of the silyl group. The new compound **34** was fully characterised.

Thermolysis of hexacarbonylchromium with **34** under the standard conditions (19 h) gave, on work-up, a modest (21%) yield of a yellow solid. Comparison of the ^{1}H NMR data to that of **34** showed that the three pyridine ring protons were shifted upfield to δ 5.67–5.28, and that the other peaks were relatively unshifted. A molecular ion *m/z* 360 (M^+ + 1) and an elemental analysis showed that the compound was tricarbonyl-[η^6-2-(2-trimethylsilyl-6-pyridyl)-1,3-dioxolane]-chromium(0) **37** (Scheme 6).



Scheme 6 *Reagents:* i, BuLi, −78 °C; ii, DMF; iii, ethylene glycol, dimethoxypropane, TsOH, PhH, reflux; iv, BuLi, −110 °C; v, TMSCl; vi, $Cr(CO)_6$, dioxane, reflux

Conclusions

The use of 2-silyl groups as temporary steric blocking protecting groups for the nitrogen lone pair of pyridine and its derivatives allows the ready preparation for the first time of a variety of tricarbonyl(η^6-pyridine)chromium(0) complexes.

Experimental

General.—All reactions and purifications involving organometallic reagents were carried out under an atmosphere of nitrogen using vacuum line and Schlenk tube techniques[16] and all solvents were deoxygenated. Glassware employed in complexation reactions was prewashed with 5% aqueous HF and thoroughly dried before use. For reactions with organic materials, no special conditions were used unless otherwise stated. All solvents were removed under reduced pressure. THF, dioxane and ether were distilled from sodium benzophenone ketyl under nitrogen and dioxane used in complexation reactions filtered through grade I alumina immediately prior to use. Light petroleum refers to the fraction boiling in the range 40–60 °C and hexane in the range 67–70 °C. Hexacarbonylchromium was steam distilled and dried and tetrabutylammonium fluoride was Fluka purum grade. Butyllithium was used as a 1.4M or 2.5M solution in hexane and lithium diisopropylamide as a 1.5M solution in cyclohexane. All other reagents were used as received or purified by standard methods.[17] Flash chromatography was performed on silica gel (43–60 μm) under a positive nitrogen pressure.

^{1}H NMR spectra were recorded in deuteriochloroform on a Brüker WH 300 spectrometer at 300.13 MHz. ^{13}C NMR spectra were recorded on a Brüker AM 250 (62.9 MHz) or Varian Gemini (50.3 MHz) spectrometers. *J* Values are in Hz. IR spectra were obtained as chloroform solutions in 0.1 mm cells on a Perkin-Elmer 781 instrument calibrated against polystyrene (1601 cm^{-1}) unless otherwise stated and for clarity only salient, characteristic peaks are noted. Mass spectra were obtained using electron impact or chemical ionisation techniques. M.p.s were obtained on a Gallenkamp hot-stage melting point apparatus and are uncorrected. Elemental analyses were obtained by the Dyson Perrins analytical department.

Standard Complexation Procedure for the Preparation of Tricarbonyl(η^6-pyridine)chromium(0) complexes.—A deoxygenated mixture of the relevant pyridine and a 1.5 molar excess of hexacarbonylchromium were heated in refluxing dioxane (15 ml per 1 g of hexacarbonyl) under a nitrogen atmosphere in the dark until greenish brown precipitates were present (17–30 h). The mixture was allowed to cool and the solution decanted from the excess of hexacarbonylchromium; it was then filtered through grade V alumina and evaporated. The residue was then subjected to flash column chromatography (eluting with a light petroleum–ether solvent system), any unchanged starting material being eluted first and the corresponding chromium complex being isolated as an amber yellow solid or oil. Further purification by recrystallisation was carried out where necessary.

Standard Desilylation Procedure.—To a solution of the relevant tricarbonyl(η^6-silylpyridine)chromium(0) complex in THF at −78 °C was added tetrabutylammonium fluoride and water. The reaction mixture was stirred, protected from light, warmed (20 °C) and the stirring continued (1–1.5 h). Removal of solvent gave a dark oil which was IMMEDIATELY flash chromatographed; elution with a light petroleum–ether solvent system followed by evaporation of solvents afforded the corresponding tricarbonyl(pyridine)chromium(0) complex as a yellow solid or oil. The product was further purified where necessary by recrystallisation.

2,6-*Bis(trimethylsilyl)pyridine* **3**.[6]—2,6-Dibromopyridine **4** (25 g, 105 mmol) was added as a solid to butyllithium (137.5 ml, 220 mmol) in dry ether (200 ml) under nitrogen and the mixture stirred (−78 °C; 1.5 h). Trimethylsilyl chloride (24 g, 220 mmol) in ether (20 ml) was added dropwise, the mixture allowed to warm (20 °C) and stirring continued overnight. The resulting light tan suspension was filtered through Celite and solvent evaporated to give a yellow oil. Distillation gave **3** as a colourless oil (21.3 g, 91%); b.p. 92 °C at 10 mmHg (lit.,[6] 123 °C at 25 mmHg); δ_H 7.49–7.40 (3 H, m, ArH), 0.33 (18 H, s, TMS) [lit.,[6] δ_H 7.31 (3 H, s, ArH) and 0.29 (18 H, s, TMS)].

Tricarbonyl[η^6-2,6-*bis(trimethylsilyl)pyridine*]*chromium*(0) **2**.—2,6-Bis(trimethylsilyl)pyridine **3** (2 g, 9.4 mmol) was complexed with hexacarbonylchromium under the standard conditions (30 h) to give **2** as a yellow oil (eluent: 15:1) that crystallised on prolonged pumping under vacuum to an amber crystalline solid (2.53 g, 75%); m.p. 68 °C; ν_{max}/cm^{-1} 1980 and 1905 (CO); δ_H 5.48 (2 H, d, *J* 6.4, 3-H and 5-H), 5.29 (1 H, t, *J* 6.4, 4-H) and 0.33 (18 H, s, TMS); *m/z* 360 (M^+ + 1) (Found: C, 47.0; H, 5.9; N, 3.9. $C_{14}H_{21}CrNO_3Si_2$ requires C, 46.8; H, 5.9; N, 3.9%).

Tricarbonyl(η^6-pyridine)chromium(0) **1**.—To tricarbonyl[η^6-2,6-bis(trimethylsilyl)pyridine]chromium **2** (400 mg, 1.1 mmol)

in THF (20 ml) was added tetrabutylammonium fluoride (788 mg, 2.5 mmol) and water (8 drops) under the standard desilylation conditions to afford **1** as a microcrystalline yellow solid (eluent: ether). Recrystallisation from isopentane gave **1** as yellow needles (205 mg, 86%); m.p. 70–73 °C (decomp.); ν_{max}/cm^{-1} 1985 and 1920 (CO); δ_H 6.56 (2 H, dt, *J* 1.4 and 3.5, 2-H and 6-H), 5.65 (1 H, tt, *J* 1.4 and 6.4, 4-H), 5.26 (2 H, m, 3-H and 5-H); *m/z* 215 (M^+) (Found: C, 44.4; H, 2.3; N, 6.2. $C_8H_5CrNO_3$ requires C, 44.7; H, 2.3; N, 6.5%).

2-t-*Butyldimethylsilylpyridine* **6**.—2-Bromopyridine **7** (7.9 g, 50 mmol) in ether (10 ml) was added dropwise to butyllithium (20 ml, 50 mmol) in ether (40 ml) at −78 °C under nitrogen and stirred (1 h). t-Butyldimethylsilyl chloride (7.55 g, 50 mmol) in ether (20 ml) was added dropwise and the solution warmed (20 °C) and stirring continued (24 h) give a light tan suspension. Filtration through Celite and removal of solvent gave a brown residue which was distilled to give **6** as a colourless oil (5.1 g, 51%); b.p. 110 °C at 10 mmHg; ν_{max}(film)/cm^{-1} 1245 (CSi). δ_H 8.71 (1 H, d, *J* 3.8, 6-H), 7.22 (1 H, d, *J* 7.5, 3-H), 7.06 (1 H, dt, *J* 1.5 and 7.5, 4-H), 6.68 (1 H, m, 5-H), 1.01 (9 H, s, Bu^t), 0.35 (6 H, s, $SiMe_2$); $\delta_C[^1H]$ 166.7, 149.8, 133.2, 129.6, 122.3, 26.3 (3 C), 16.6 and −6.7 (6 C); *m/z* 194 ($M^+ + 1$) (Found: C. 68.3; H, 10.25; N, 7.5. $C_{11}H_{19}NSi$ requires C, 68.3; H, 9.9; N, 7.2%).

(η^6-2-t-*Butyldimethylsilylpyridine*)*tricarbonylchromium*(0) **8**.—2-t-Butyldimethylsilylpyridine **6** (1 g, 5.18 mmol) was complexed under the standard condtions (19 h) to give **8** as a yellow powder (eluent: 4:1). Crystallisation from isopentane gave **8** as yellow blocks (340 mg, 20%); m.p. 94 °C; ν_{max}/cm^{-1} 1985 and 1912 (CO); δ_H 6.68 (1 H, d, *J* 4.0, 6-H), 5.53 (1 H, m, 4-H), 5.35 (1 H, m, 3-H), 5.24 (1 H, d, *J* 6.4, 3-H), 0.92 (9 H, s, Bu^t), 0.38 (3 H, s, SiMe) and 0.32 (3 H, s, SiMe); *m/z* 329 (M^+) (Found: C, 51.25; H, 6.1; N, 4.2. $C_{14}H_{19}CrNO_3Si$ requires C. 51.05; H, 5.8; N, 4.25%).

Desilylation of (η^6-2-t-*Butyldimethylsilylpyridine*)*tricarbonylchromium*(0) **8**.—To (η^6-2-t-butyldimethylsilylpyridine)tricarbonylchromium(0) **8** (50 mg, 0.152 mmol) in THF (5 ml) was added tetrabutylammonium fluoride (60 mg, 0.19 mmol) along with water (3 drops) under the standard conditions (eluent: ether) to give tricarbonyl(η^6-pyridine)chromium(0) **1** as a yellow solid (31 mg, 95%), identical in all respects with the previously prepared sample.

2-t-*Butyldimethylsilyl*-5-*methylpyridine* **12**.—2-Bromo-5-methylpyridine **11**[8,18] (4.0 g, 23.2 mmol) in THF (10 ml) was added to butyllithium (10 ml, 25 mmol) in THF (10 ml) at −78 °C under nitrogen and stirred (1 h). t-Butyldimethylsilyl chloride (3.62 g. 24 mmol) in THF (10 ml) was added and the mixture warmed (20 °C) and stirred (16 h). It was then evaporated and the residue extracted with ether. The extract was filtered through Celite and the eluate evaporated to give an oil which upon distillation gave **12** as a colourless oil; this solidified with time to give white crystals (4.05 g, 84%); m.p. 28 °C: ν_{max}/cm^{-1} 1249 (CSi); δ_H 8.63 (1 H, s, 2-H), 7.39 (2 H, d, *J* 1.5, 4-H and 5-H), 2.32 (3 H, s, 5-Me), 0.92 (9 H, s, Bu^t), 0.35 (6 H, s, $SiMe_2$); $\delta_C[^1H]$ 162.7, 150.6, 134.1, 131.9, 129.5, 26.5 (3 C), 25.7 and −6.3 (2 C); *m/z* 208 ($M^+ + 1$) (Found: C, 69.2; H, 10.6; N. 6.5. $C_{12}H_{21}NSi$ requires C, 69.5; H, 10.2; N, 6.75%).

(η^6-2-t-*Butyldimethylsilyl*-5-*methylpyridine*)*tricarbonylchromium* **13**.—2-t-Butyldimethylsilyl-5-methylpyridine **12** (1.0 g, 4.8 mmol) was complexed under the standard conditions (19 h) to afford **13** as a yellow powder (eluent: 3:1). Crystallisation from pentane gave **13** as yellow blocks (477 mg, 29%); m.p. 64 °C: ν_{max}/cm^{-1} 1980 and 1905 (CO); δ_H 6.51 (1 H, s, 2-H), 5.36 (2 H, d, *J* 1.3, 4-H and 5-H), 2.23 (3 H, s, 5-Me), 0.92 (9 H, s, Bu^t), 0.37 (3 H, s, SiMe) and 0.30 (3 H, s, SiMe); *m/z* 343 (M^+) (Found: C, 52.3; H, 6.3; N, 4.0. $C_{15}H_{21}CrNO_3Si$ requires C, 52.5; H, 6.2; N, 4.1%).

Tricarbonyl(η^6-3-*methylpyridine*)*chromium*(0) **9**.—To (η^6-2-t-butyldimethylsilyl-5-methylpyridine)tricarbonylchromium(0) **13** (200 mg, 0.58 mmol) in THF (25 ml, −78 °C) was added tetrabutylammonium fluoride (252 mg, 0.8 mmol) and water (8 drops) under standard desilylation conditions which afforded **9** as a crystalline yellow solid (eluent: ether). Recrystallisation from CH_2Cl_2–hexane gave yellow blocks (110 mg, 83%); m.p. 80–83 °C (decomp.); ν_{max}/cm^{-1} 1981 and 1910 (CO); δ_H 6.47 (1 H, d, *J* 1.5, 2-H), 6.43 (1 H, dd, *J* 1.2 and 4.0, 6-H), 5.54 (1 H, d, *J* 6.5, 4-H), 5.29 (1 H, dd, *J* 4.0 and 6.5, 5-H) and 2.19 (3 H, s, 3-Me); *m/z* 230 ($M^+ + 1$) (Found: C, 47.3; H, 3.1; N, 6.1. $C_9H_7CrNO_3$ requires C, 47.2; H, 3.1; N, 6.1%).

2-*t-Butyldimethylsilyl*-3-*methylpyridine* **14**.—2-Bromo-3-methylpyridine **16**[8,19] (4.0 g, 23.2 mmol) in THF (10 ml) was added to butyllithium (10 ml, 25 mmol) in THF (10 ml) at −78 °C under nitrogen and the mixture stirred (1 h). t-Butyldimethylsilyl triflate (6.33 g, 24 mmol) in THF (10 ml) was added slowly and stirring continued (−78 °C; 2 h); the mixture was then warmed (20 °C) and stirred for a further 16 h. After this it was evaporated and the residue extracted with hexane; filtration of the extract through Celite and evaporation of the eluate gave an oil which upon distillation gave **14** as a colourless oil (4.22 g, 87.5%); b.p. 88–93 °C at 0.1 mmHg; ν_{max}(film)/cm^{-1} 1249 (CSi); δ_H 8.59 (1 H, d, *J* 4.6, 6-H), 7.33 (1 H, d, *J* 5.5, 4-H), 7.07 (1 H, dd, *J* 4.6 and 5.5, 3-H), 2.42 (3 H, s, 3-Me), 0.93 (9 H, s, Bu^t), 0.39 (6 H, s, $SiMe_2$); $\delta_C[^1H]$ 165.1, 146.7, 140.0, 135.9, 122.2, 26.7, 21.2, 18.0 (3 C) and 3.8 (2 C); *m/z* 208 ($M^+ + 1$) (Found: C, 69.5; H, 10.5. $C_{12}H_{21}NSi$ requires C, 69.5; H, 10.2%).

(η^6-2-*t-Butyldimethylsilyl*-3-*methylpyridine*)*tricarbonylchromium*(0) **17**.—2-t-Butyldimethylsilyl-3-methylpyridine **14** (1.0 g, 4.8 mmol) was complexed under the standard conditions (17 h) to afford **17** as a yellow oil (eluent: 4:1). Crystallisation from pentane gave **17** as yellow blocks (461 mg, 28%); m.p. 56 °C; ν_{max}/cm^{-1} 1982 and 1910 (CO); δ_H 6.53 (1 H, dd, *J* 1.3 and 3.9, 2-H), 5.47 (1 H, dd, *J* 3.9 and 6.5, 5-H), 5.30 (1 H, d, *J* 6.5, 4-H), 2.22 (3 H, s, 3-Me), 0.94 (9 H, s, Bu^t), 0.55 (3 H, s, SiMe) and 0.31 (3 H, s, SiMe); *m/z* 343 (M^+) (Found: C, 52.2; H, 6.45; N, 4.4. $C_{15}H_{21}CrNO_3Si$ requires C, 52.5; H. 6.2; N, 4.1%).

Desilylation of (η^6-*t-Butyldimethylsilyl*-3-*methylpyridine*)*tricarbonylchromium*(0) **17**.—To (η^6-2-t-butyldimethylsilyl-3-methylpyridine)tricarbonylchromium **17** (50 mg, 0.145 mmol) in THF (10 ml) was added tetrabutylammonium fluoride (63 mg, 0.2 mmol) and water (2 drops) under the standard conditions (eluent: ether) to afford tricarbonyl(η^6-3-methylpyridine)chromium **9** (28 mg, 85%) as a crystalline yellow solid, identical with a previously prepared sample.

6-*Methyl*-2-*trimethylsilylpyridine* **18**.—2-Bromo-6-methylpyridine **20**[8,20] (20 g, 116 mmol) was added as a solution in ether (40 ml) to butyllithium (48 ml, 120 mmol) in ether (70 ml) at −78 °C under nitrogen and stirred (1 h). Trimethylsilyl chloride (13.0 g, 120 mmol) in ether (20 ml) was added dropwise and the solution warmed (20 °C) and stirring continued (24 h) to give an off white suspension. Filtration of this through Celite and removal of solvent gave a brown residue which was distilled to give **18** as a colourless oil (13.82 g, 72.5%); b.p. 81 °C at 11 mmHg) (lit.,[9] 199 °C at 753 mmHg); δ_H 7.45 (1 H, t, *J* 7.5, 4-H), 7.30 (1 H, d, *J* 7.5, 3-H), 7.05 (1 H. d, *J* 7.5, 5-H), 2.59 (3 H, s, 6-Me) and 0.33 (9 H, s, TMS).

Tricarbonyl(η⁶-2-*trimethylsilyl*-6-*methylpyridine*)-*chromium*(0) **21**.—Trimethylsilyl-6-methylpyridine **18** (2 g, 9.4 mmol) was complexed under the standard conditions (19 h) to give **21** as a yellow powder (eluent: 5:1). Crystallisation of this from isopentane gave **21** as yellow blocks (1.19 g, 42%); m.p. 49 °C; ν_{max}/cm^{-1} 1980 and 1905 (CO); δ_H 5.58 (1 H, t, *J* 6.5, 4-H), 5.30 (1 H, d, *J* 6.5, 3-H), 5.14 (1 H, d, *J* 6.5, 5-H), 5.24 (1 H, d, *J* 6.4, 3-H), 2.41 (3 H, s, 6-Me) and 0.35 (9 H, s, TMS); *m/z* 301 (M^+) (Found: C, 48.4; H, 5.0; N, 4.5. $C_{12}H_{15}CrNO_3Si$ requires C, 48.1; H, 5.0; N, 4.65%).

Tricarbonyl(η⁶-2-*methylpyridine*)*chromium*(0) **22**.[2]—To tricarbonyl(η⁶-2-trimethylsilyl-6-methylpyridine)chromium(0) **21** (700 mg, 2.32 mmol) in THF (25 ml) was added tetrabutylammonium fluoride (756 mg, 2.4 mmol) and water (8 drops) under standard desilylation conditions to afford **22** as a microcrystalline yellow solid (eluent: 1:4). Recrystallisation from isopentane gave golden yellow blocks (499 mg, 94%); m.p. 63 °C (decomp.); ν_{max}/cm^{-1} 1983 and 1910 (CO); δ_H 6.60 (1 H, d, *J* 3.6, 6-H), 5.66 (1 H, dt, *J* 1.6 and 6.5, 4-H), 5.22 (2 H, d, *J* 6.5, 3-H), 5.15 (1 H, m, 5-H) and 2.42 (3 H, s, 2-Me); *m/z* 229 (M^+) (Found: C, 47.0; H, 3.1; N, 6.0. $C_9H_7CrNO_3$ requires C, 47.2; H, 3.1; N, 6.1%).

2-*Bromo*-6-*ethylpyridine* **23**.—2-Bromo-6-methylpyridine **20** (20 g, 116 mmol) was added as a solution in THF (40 ml) to lithium diisopropylamide (80 ml, 120 mmol) in THF (50 ml) at −78 °C under nitrogen slowly with stirring to give a deep red solution. Stirring was continued (0.5 h) and methyl iodide (17.4 g, 120 mmol) in THF (20 ml) added. The solution was warmed (20 °C) and stirring continued (18 h), to give a light, clear solution. Solvent was removed and the residue dissolved in ether and the solution washed with aqueous NaOH, separated and the aqueous layer extracted with ether (4 × 100 ml). The combined extracts were dried (KOH) and evaporated and the residue distilled to give **23** as a colourless oil (17.97 g, 83%); b.p. 59 °C at 0.5 mmHg; ν_{max}(film)/cm^{-1} 2980, 1590, 1505, 1459 and 803; δ_H 7.43 (1 H, t, *J* 7.7, 4-H), 7.27 (1 H, d, *J* 7.7, 3-H), 7.08 (1 H, d, *J* 7.7, 5-H), 2.77 (2 H, q, *J* 7.6, C*H*$_2$Me), 1.27 (3 H, t, *J* 7.6, CH$_2$*Me*); δ_C[^{1}H] 165.2, 141.5, 138.5, 125.1, 120.6, 40.0 and 13.6; *m/z* 185 and 187 (M^+) (Found: C, 45.5: H, 4.55; N, 7.8. C_7H_8BrN requires C, 45.2; H, 4.3; N, 7.5%).

2-*Bromo*-6-(*but*-3-*enyl*)*pyridine* **24**.—2-Bromo-6-methylpyridine **20** (20 g, 116 mmol) was lithiated as above to give a deep red solution which was stirred for 0.5 h. Allyl bromide (14.52 g, 120 mmol) in THF (20 ml) was then added and the solution warmed (20 °C) and stirring continued (18 h), to give a light, clear solution. The latter was evaporated and the residue dissolved in ether, and the solution washed with aqueous NaOH and separated. The aqueous layer was then extracted with ether (4 × 100 ml) and the combined extracts were dried (KOH). Removal of solvent and distillation of the residue gave **24** as a colourless oil (16.79 g, 68%); b.p. 91 °C at 0.5 mmHg; ν_{max}(film)/cm^{-1} 1590, 1561, 1448 and 910; δ_H 7.44 (1 H, t, *J* 7.6, 4-H), 7.30 (1 H, d, *J* 7.6, 3-H), 7.09 (1 H, d, *J* 7.6, 5-H), 5.80 (1 H, m, C*H*=CH$_2$), 5.07–4.95 (2 H, m, CH=CH$_2$), 2.85 (2 H, t, *J* 7.4, C*H*$_2$CH$_2$CH=CH$_2$), 2.47 (2 H, m, CH$_2$C*H*$_2$CH=CH$_2$); δ_C[^{1}H] 163.1, 141.5, 138.5, 133.2 (2 C), 121.5, 115.3, 37.2 and 33.4; *m/z* 211 and 213 (M^+) (Found: C, 51.1; H, 5.1; N, 6.2. $C_9H_{10}BrN$ requires C, 51.1; H, 4.75; N, 6.6%.

6-*Ethyl*-2-*trimethylsilylpyridine* **25**.—2-Bromo-6-ethylpyridine **23** (5 g, 27 mmol) in dry ether (10 ml) was added to butyllithium (10.8 ml, 27 mmol) in dry ether at −78 °C under nitrogen and the solution stirred (1 h). Trimethylsilyl chloride (3.02 g, 28 mmol) in dry ether was added dropwise and stirring continued (10 min). The solution was warmed (20 °C) and stirred for further 16 h to give a white suspension. The latter was filtered through Celite, the eluate evaporated, and the resultant yellow oil distilled to give **25** as a colourless oil (4.51 g, 86%); b.p. 90 °C at 12 mmHg; ν_{max}(film)/cm^{-1} 1248 (CSi); δ_H 7.49 (1 H, t, *J* 7.5, 4-H), 7.31 (1 H, d, *J* 7.5, 3-H), 7.05 (1 H, d, *J* 7.5, 5-H), 2.86 (2 H, q, *J* 7.6 C*H*$_2$Me), 1.29 (3 H, t, CH$_2$*Me*) and 0.32 (9 H, s, TMS); δ_C[^{1}H] 167.5, 163.2, 133.9, 125.7, 120.8, 31.7, 13.8 and −1.7 (3 C); *m/z* 179 (M^+) (Found: C, 66.9; H, 9.6; N, 8.0. $C_{10}H_{17}NSi$ requires C, 67.0; H, 9.55; N, 7.8%).

6-(*But*-3-*enyl*)-2-*trimethylsilylpyridine* **26**.—2-Bromo-6-(but-3-enyl)pyridine **68** (5 g, 23.6 mmol) was lithiated with butyllithium (10 ml, 25 mmol) as above and quenched with trimethylsilyl chloride (2.70 g, 25 mmol) in the same way as **23** above to afford **26** as a colourless oil (4.02 g, 87%); b.p. 75 °C at 0.5 mmHg; ν_{max}(film) cm^{-1} 1246 (C-Si); δ_H 7.46 (1 H, t, *J* 7.5, 4-H), 7.30 (1 H, dd, *J* 0.9 and 7.5, 3-H), 7.01 (1 H, dd, *J* 0.9 and 7.5, 5-H), 5.90 (1 H, m, C*H*=CH$_2$), 5.08–4.95 (2 H, m, CH=C*H*$_2$), 2.90 (2 H, t, *J* 7.4, C*H*$_2$CH$_2$CH=CH$_2$), 2.53 (2 H, m, CH$_2$C*H*$_2$CH=CH$_2$) and 0.31 (9 H, s, TMS); δ_C[^{1}H] 167.6, 161.1, 138.4, 133.8, 125.8, 121.6, 114.6, 37.8, 33.5 and −1.8 (3 C); *m/z* 206 (M^+ + 1) (Found: C, 70.5; H, 9.4; N, 6.8. $C_{12}H_{19}NSi$ requires C, 70.2; H, 9.3; N, 6.8%.

Tricarbonyl(η⁶-*ethyl*-2-*trimethylsilylpyridine*)*chromium*(0) **27**.—6-Ethyl-2-trimethylsilylpyridine **25** (1 g, 5.6 mmol) was complexed according to the standard procedure (19 h) to afford **27** as a yellow oil (eluent: 7:1) (847 mg, 48%); ν_{max}/cm^{-1} 1980 and 1901 (CO) cm^{-1}; δ_H 5.57 (1 H, t, *J* 6.6, 4-H), 5.32 (1 H, d, *J* 6.6, 3-H), 5.19 (1 H, d, *J* 6.6, 5-H), 2.66 (2 H, q, *J* 7.5, C*H*$_2$Me), 1.27 (3 H, t, *J* 7.5 CH$_2$*Me*) and 0.35 (9 H, s, TMS); *m/z* 315 (M^+) (Found: C, 49.3; H, 5.4; N, 4.3. $C_{13}H_{17}CrNO_3Si$ requires C, 49.5; H, 5.4; N, 4.4%).

[η⁶-6-(*But*-3-*enyl*)-2-*trimethylsilylpyridine*]*tricarbonyl*-*chromium*(0) **28**.—6-(But-3-enyl)-2-trimethylsilylpyridine **26** (1.48 g, 7.2 mmol) was complexed according to the standard procedure (18 h) to afford **28** as a yellow oil (eluent: 7:1) (1.0 g, 41%); ν_{max}/cm^{-1} 1972 and 1900 (CO); δ_H 5.95 (1 H, m, C*H*=CH$_2$), 5.56 (1 H, t, *J* 6.5, 4-H), 5.32 (1 H, d, *J* 6.5, 3-H), 5.19 (1 H, d, *J* 6.5, 5-H), 5.09–4.99 (2 H, m, CH=C*H*$_2$), 2.73 (2 H, m, C*H*$_2$CH$_2$CH=CH$_2$), 2.44 (2 H, q, *J* 6.9, CH$_2$C*H*$_2$CH=CH$_2$) and 0.35 (9 H, s, TMS); *m/z* 342 (M^+ + 1) (Found: C, 52.8; H, 5.9; N, 4.0. $C_{15}H_{19}CrNO_3Si$ requires C, 52.8; H, 5.6; N, 4.1%).

Tricarbonyl(η⁶-2-*ethylpyridine*)*chromium*(0) **29**.—To tricarbonyl(η⁶-6-ethyl-2-trimethylsilylpyridine)chromium(0) **27** (400 mg, 1.27 mmol) in THF (20 ml) was added tetrabutylammonium fluoride (630 mg, 2.0 mmol) and water (8 drops) under standard desilylation conditions which gave **29** as a yellow oil (eluent: 1:2). Crystallisation from isopentane gave yellow plates (290 mg, 94%); m.p. 52 °C; ν_{max}/cm^{-1} 1988 and 1919 (CO); δ_H 6.62 (1 H, d, *J* 4.0, 6-H), 5.67 (1 H, dt, *J* 1.5 and 6.4, 4-H), 5.23 (1 H, d, *J* 6.4, 3-H), 5.18 (1 H, m, 5-H), 2.67 (2 H, dq, *J* 1.2 and 7.5, CH$_2$Me), 1.29 (3 H, t, *J* 7.5, CH$_2$Me); *m/z* 243 (M^+) (Found: C, 49.3; H, 3.5; N, 5.5. $C_{10}H_9CrNO_3$ requires C, 49.4; H, 3.7; N, 5.8%).

[η⁶-2-(*But*-3-*enyl*)*pyridine*]*tricarbonylchromium*(0) **30**.—To [η⁶-6-(But-3-enyl)-2-trimethylsilylpyridine]tricarbonylchromium(0) **28** (300 mg, 0.96 mmol) in THF (20 ml) was added tetrabutylammonium fluoride (630 mg, 2.0 mmol) and water (8 drops) under the standard desilylation conditions which afforded **30** as a yellow oil (eluent: 1:1) (238 mg, 92%); ν_{max}/cm^{-1} 1985 and 1915 (CO); δ_H 6.61 (1 H, d, *J* 4, 6-H), 5.85 (1 H, m, C*H*=CH$_2$) 5.66 (1 H, dt, *J* 1.5 and 6.5, 4-H), 5.21 (1 H, d, *J* 6.5, 3-H), 5.16 (1 H, m, 5-H), 5.10–5.01 (2 H, m, CH=C*H*$_2$),

2.70 (2 H, t, *J* 7, $CH_2CH_2CH{=}CH_2$) and 2.44 (2 H, m, $CH_2CH_2CH{=}CH_2$); *m/z* 270 ($M^+ + 1$) (Found: C, 53.6; H, 4.1; N, 5.15. $C_{12}H_{11}CrNO_3$ requires C, 53.5; H, 4.1; N, 5.2%).

Reaction of Complex **1** *with Lithium Diisopropylamide and Methyl Iodide.*—Tricarbonyl(η^6-pyridine)chromium(0) **1** (100 mg, 0.465 mmol) in THF (5 ml) was added slowly dropwise to lithium diisopropylamide (0.4 ml, 0.6 mmol) in THF (10 ml) at −40 °C with stirring to give a deep orange solution. The solution was stirred (−40 °C; 1 h) whilst methyl iodide was added (44 μl, 0.7 mmol) and was then further stirred (−40 °C; 0.5 h). After this it was warmed (20 °C) and stirred for a further 2 h. The mixture was then evaporated and residue extracted (CH_2Cl_2; 10 ml). The extract was filtered through alumina and the eluate evaporated to give a yellow–brown gum. Chromatography, eluting with light petroleum–ether (1:3) gave on evaporation tricarbonyl(η^6-2-methylpyridine)chromium(0) **22** (72 mg, 68%), identical in all respects with the previously prepared sample.

Tricarbonyl[η^6-4-*methyl*-2,6-*bis*(*trimethylsilyl*)*pyridine*]-*chromium*(0) **32**.—Tricarbonyl[η^6-2,6-bis(trimethylsilyl)pyridine]chromium **2** (300 mg, 0.83 mmol) in THF (5 ml) was added dropwise to lithium diisopropylamide (1 ml, 1.5 mmol) in THF (20 ml) at −40 °C and the mixture stirred (2 h). Methyl iodide (0.2 ml) was then added and the stirring continued (3 h). After this the mixture was warmed (20 °C) and the solvents evaporated. The residue was extracted (CH_2Cl_2; 10 ml) and the extract evaporated to provide an oil; chromatography of this, eluting with light petroleum–ether (8:1) gave on evaporation **32** as yellow crystals (225 mg, 73%); m.p. 58–59 °C; ν_{max}/cm^{-1} 1971 and 1900 (CO); δ_H 5.28 (2 H, s, 3-H and 5-H), 2.09 (3 H, s, 4-Me), 0.33 (18 H, s, TMS); *m/z* 373 (M^+) (Found: C, 48.05; H, 6.4; N, 3.5. $C_{15}H_{23}CrNO_3Si_2$ requires C, 48.2; H, 6.2; N, 3.75%).

Tricarbonyl(η^6-4-*methylpyridine*)*chromium*(0) **33**.—To tricarbonyl[η^6-4-methyl-2,6-bis(trimethylsilyl)pyridine]-chromium(0) **32** (200 mg, 0.53 mmol) in THF (15 ml; −78 °C) was added tetrabutylammonium fluoride (422 mg, 1.34 mmol) and water (7 drops) under standard desilylation conditions to afford **33** as a crystalline yellow solid (eluent: ether). Recrystallisation from CH_2Cl_2–hexane gave yellow blocks (93 mg, 76%); m.p. 53 °C (decomp.); ν_{max}/cm^{-1} 1989 and 1916 (CO); δ_H 6.58 (2 H, d, *J* 4.7, 2-H and 6-H), 5.15 (2 H, d, *J* 4.7, 3-H and 5-H) and 2.21 (3 H, s, 4-Me); *m/z* 229 (M^+) (Found: C, 47.1; H, 3.0; N, 5.8. $C_9H_7CrNO_3$ requires C, 47.2; H, 3.1; N, 6.1%).

2-(2-*Trimethylsilyl*-6-*pyridyl*)-1,3-*dioxolane* **34**.—A solution of 2-(2-bromo-6-pyridyl)-1,3-dioxolane **35**[15] (3.0 g, 13.5 mmol) in ether (20 ml) was added to butyllithium (9.6 ml, 13.5 mmol) at −110 °C under nitrogen over 10 min with stirring. The mixture was warmed (−78 °C; 0.5 h), cooled (−100 °C) and trimethylsilyl chloride (1.47 g, 13.2 mmol) added. The mixture was then stirred (1 h) after which it was warmed (20 °C) and further stirred (24 h). It was then filtered through Celite and evaporated and the residue distilled to give **34** as a colourless oil (2.2 g, 73%): b.p. 104 °C at 0.1 mmHg; ν_{max}(film)/cm^{-1} 1248 (CSi); δ_H 7.62 (1 H, t, *J* 7.6, 4-H), 7.50–7.41 (2 H, m, 3-H and 5-H), 5.88 (1 H, s, OCHO), 4.23–4.06 (4 H, m, OCH_2CH_2O) and 0.32 (9 H, s, TMS); $\delta_C[^1H]$ 167.9, 157.0, 134.4, 128.8, 119.5, 104.5, 65.5 (2 C) and −1.8 (3 C); *m/z* 224 ($M^+ + 1$) (Found: C, 59.4; H, 8.0. $C_{11}H_{17}NO_2Si$ requires C, 59.2; H, 7.7%).

Tricarbonyl[η^6-2-(2-*trimethylsilyl*-6-*pyridyl*)-1,3-*dioxolane*]-*chromium*(0) **37**.—2-(2-Trimethylsilyl-6-pyridyl)-1,3-dioxolane **34** (1.0 g, 4.5 mmol) was complexed under the standard conditions (19 h) to give **37** as a yellow gum (eluent: 3:1). Crystallisation gave **37** as yellow needles (339 mg, 21%); m.p. 70 °C; ν_{max}/cm^{-1} 1993 and 1921 (CO); δ_H 5.67 (1 H, d, *J* 6.6, 3-H), 5.55 (1 H, s, OCHO), 5.54 (1 H, t, *J* 6.6, 4-H), 5.28 (1 H, d, *J* 6.6, 5-H), 4.23–4.10 (4 H, m, OCH_2CH_2O) and 0.36 (9 H, s, TMS); *m/z* 360 ($M^+ + 1$) (Found: C, 46.6; H, 4.7; N, 3.7. $C_{14}H_{17}CrNO_5Si$ requires C, 46.8; H, 4.8; N, 3.9%).

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