Tricarbonyl(pyridine)chromium Complexes: Conversion into Tricarbonyl(dihydropyridine)chromium Complexes *via* Regio- and Stereo-selective Nucleophilic Addition Reactions

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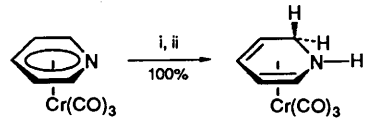
Tricarbonyl(η-pyridine)chromium undergoes reduction in the presence of diisobutylaluminium hydride (DIBAL) to afford tricarbonyl(η-1,2-dihydropyridine)chromium in essentially quantitative yield. Tricarbonyl(pyridine)chromium complexes undergo nucleophilic addition reactions with alkyllithium reagents, with subsequent methyl iodide quench, to generate tricarbonyl(η-*N*-methyl-*exo*-2-alkyl-1,2-dihydropyridine)chromium complexes with complete stereocontrol. The reaction also occurs with the corresponding 2- and 4-methylpyridine complexes, no concomitant deprotonation of the methyl protons being observed. In the case of tricarbonyl(3-methylpyridine)chromium the addition takes place preferentially at the more hindered 2-position rather than the 6-position to give a 4.1 mixture of regioisomeric complexes. The regiochemistry of the reaction can, however, be controlled by the use of removable silyl groups to block the 2- and 6-positions by utilising tricarbonyl(2-*tert*-butyldimethylsilyl-3-methylpyridine)chromium or the corresponding 2,5-isomer. These addition reactions are shown to be quite general in the nature of the pyridine complex, the alkyllithium reagent and the electrophile employed since the methyl iodide can be replaced by a proton or other alkyl halides to give analogous tricarbonyl(dihydropyridine)chromium complexes.

The electron withdrawing character of the tricarbonylchromium moiety influences the chemistry of complexed arenes by increasing the acidities of aryl[1] and benzylic[2] protons and by promoting nucleophilic additions.[3] The tricarbonylchromium moiety stabilises aryl, benzylic and cyclohexadienyl anions. Whereas the above classes of reactivity have been extensively studied for tricarbonyl(arene)chromium complexes the corresponding reactions on tricarbonyl(pyridine)chromium complexes have not been investigated due to the lack of availability of the latter. We recently reported a general synthetic method for tricarbonyl(pyridine)chromium complexes *via* complexation of 2-trimethylsilylpyridines with subsequent removal of the bulky silyl protecting groups. We now report that the reaction between tricarbonyl(η-pyridine)chromium complexes and alkyllithium reagents proceeds smoothly to afford, after electrophilic quench, tricarbonyl(η-*exo*-2-alkyl-1,2-dihydropyridine)chromium complexes. Part of this work has been the subject of a preliminary communication.[4]

Results and Discussion

Treatment of a yellow toluene solution of tricarbonyl(pyridine)chromium **1** at −78 °C with diisobutylaluminium hydride (DIBAL) resulted in an instant colour change to red. Addition of methanol and warming gave, after solvent evaporation, a red powder. Chromatography afforded a single red band which upon evaporation provided red crystals of tricarbonyl(1,2-dihydropyridine)chromium **2** in essentially quantitative yield. The ^{1}H NMR spectrum of **2** contained four 1 H multiplet resonances in the range δ 5.92–3.75 corresponding to four contiguous complexed vinyl protons along with two multiplet resonances at δ 3.66 and 3.21 due to the two diastereotopic protons at C-2 and a very broad singlet peak at δ 2.30 due to the NH proton. A sharp band in the IR spectrum at 3395 cm^{-1} indicated the presence of an NH group and three intense bands around 2000 cm^{-1} indicated the presence of the tricarbonylchromium moiety. Elemental analysis confirmed **2** as tricarbonyl(1,2-dihydropyridine)chromium (Scheme 1).

The above reaction is completely regioselective and the ready



1 **2**

Scheme 1 *Reagents:* i, DIBAL, PhMe, −78 °C; ii, MeOH

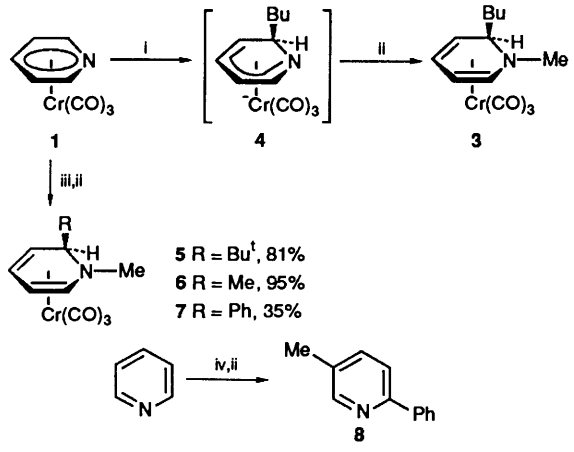
isolation of complex **2** serves to illustrate the stabilising effect of the electron-withdrawing tricarbonylchromium fragment on the electron-rich diene moiety of the 1,2-dihydropyridine: 1,2-dihydropyridine itself has not been isolated.[5]

Treatment of tricarbonyl(pyridine)chromium **1** with 1.1 equiv. of butyllithium in THF at −78 °C caused the initially yellow solution to turn orange. Stirring for 2 h, addition of methyl iodide, and warming to room temperature gave a deep blood red solution, TLC analysis of which indicated the presence of a single compound. Filtration through alumina and evaporation of solvents gave a red gum which crystallised with time. ^{1}H NMR spectroscopy revealed the presence of five 1 H multiplets at δ 5.72, 5.36, 5.17, 3.94 and 3.47, a 3 H singlet at δ 2.58 characteristic of an *N*-methyl group and a 9 H multiplet consistent with a butyl side chain. The IR spectrum contained peaks at 1950, 1870 and 1828 cm^{-1} which showed that the tricarbonylchromium moiety was still present. Recrystallisation of the material gave deep blood red blocks whose mass spectrum contained a molecular ion *m*/*z* (M^+ 279) which suggested, along with the ^{1}H NMR data, that the product was tricarbonyl(η-*exo*-2-butyl-*N*-methyl-1,2-dihydropyridine)-chromium **3** (in 98% yield) derived from initial attack of butyllithium at the 2-position followed by methylation of the resultant dienaminyl anion **4** on nitrogen. In line with other nucleophilic addition reactions to tricarbonyl(arene)chromium complexes, addition was assumed to have taken place away from the tricarbonylchromium moiety to give the *exo*-isomer.[6] An elemental analysis confirmed that addition had taken place.

The above reaction was repeated with *tert*-butyllithium, methyllithium and phenyllithium as nucleophiles; in each case analogous products were obtained on methylation as single *exo*-diastereoisomers **5**, **6** and **7**. In none of these reactions was

there any evidence that deprotonation of **1** or addition to the 3- or 4-positions was occurring. These new compounds all gave satisfactory spectroscopic data and correct elemental analyses.

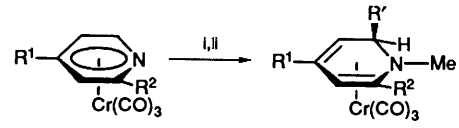
These reactions are remarkable since attack of alkyllithium reagents on pyridine itself can have a variety of different outcomes. For example, treatment of pyridine with phenyllithium followed by methyl iodide gives 5-methyl-2-phenylpyridine **8**[7] but treatment with other alkyllithium reagents often gives a multiplicity of products. The nature of these products (being isomers of the mono-, di- and tri-substituted alkylpyridines) depends on the conditions used which, in general, are more forcing than those used in the above sequence of reactions (Scheme 2).[8]



Scheme 2 *Reagents:* i, BuLi, −78 °C; ii, MeI; iii, RLi, −78 °C; iv, PhLi, 0 °C

With the preliminary results on complex 1 in hand, it was now of interest to investigate the above reaction on substituted tricarbonyl(pyridine)chromium complexes to see whether the introduction of a side chain would affect the reactivity. The above reactions were repeated, this time using tricarbonyl(η-2-*tert*-butyldimethylsilylpyridine)chromium **9**. Treatment of **9** with butyllithium and methyl iodide gave a red product which by ^{1}H NMR spectroscopy still retained the *tert*-butyldimethylsilyl group, since there was a 9 H singlet due to the *tert*-butyl group and two 3 H singlets due to the diastereotopic methyl groups. Also present were four 1 H multiplets, an *N*-methyl singlet and a 9 H multiplet. This, along with a molecular ion *m/z* ($M^+ + 1$) 402 and a correct elemental analysis showed the complex to be tricarbonyl(η-6-*tert*-butyldimethylsilyl-*N*-methyl-*exo*-2-butyl-1,2-dihydropyridine)chromium **10**. Repetition of the reaction with *tert*-butyllithium, methyllithium and phenyllithium all gave analogous products **11**, **12** and **13** showing that the presence of the silyl group did not hinder, and was unaffected by, the reaction.

Where the pyridine ring bears a methyl group at the 2- or 4-position, the normal acidity of these methyl protons, enhanced by complexation to tricarbonylchromium should make removal of such protons relatively facile. However, treatment of tricarbonyl(η-2-methylpyridine)chromium **14** with the same set of alkyllithium reagents as before followed by quenching with methyl iodide gave tricarbonyl(η-dihydropyridine)chromium complexes **15**–**18** as red crystalline solids in good to excellent yield. In each case there was no sign of deprotonation of the methyl group and only clean addition of the alkyllithium to the vacant 6-position was observed. The reaction produced similar results when performed on tricarbonyl(η-4-methylpyridine)-chromium **19**, addition of the nucleophile again occurring at the 2-position with no interference from the methyl group to give the appropriately substituted tricarbonyl(dihydropyridine)-chromium complexes **20**–**23**. These two sets of results show that the susceptibility of the complexed pyridine ring is such that the nucleophilic addition reaction is completely favoured over any deprotonation reaction with reagents such as alkyllithiums. This is at variance with the reaction of uncomplexed alkylpyridines with even relatively strong nucleophilic bases whereby a methyl group at either the 2- or 4-position undergoes metallation with no concomitant attack on the pyridine ring itself[9] (Scheme 3).



9 R^1 = H, R^2 = TBDMS — **10** R' = Bu, 99%; **11** R' = Bu^t, 81%; **12** R' = Me, 98%; **13** R' = Ph, 93%

14 R^1 = H, R^2 = Me — **15** R' = Bu, 96%; **16** R' = Bu^t, 70%; **17** R' = Me, 80%; **18** R' = Ph, 79%

19 R^1 = Me, R^2 = H — **20** R' = Bu, 92%; **21** R' = Bu^t, 64%; **22** R' = Me, 91%; **23** R' = Ph, 43%

Scheme 3 *Reagents:* i, R'Li, −78 °C; ii, MeI

Tricarbonyl(η-3-methylpyridine)chromium **24** differs from all the previous cases so far discussed in that there are now two distinct 2- and 6-positions and, in principle, addition to either of these sites could occur. Treatment of **24** with methyllithium under the same conditions as above with methyl iodide quench gave a red solution as before. Filtration of the reaction mixture through alumina and evaporation of solvents yielded a red gum which, by virtue of two sets of resonances in the ^{1}H NMR spectrum, was shown to consist of two compounds, which were inseparable by chromatography. The presence of two methyl doublets at δ 0.62 and 0.60 and two methyl singlets at δ 2.57 and 2.50 in the ratio 80:20 along with other 1 H resonances and a molecular ion *m/z* 259 (M^+) allowed identification of the mixture as an 80:20 mixture of tricarbonyl(η-*exo*-*N*,2,3-trimethyl-1,2-dihydropyridine)chromium **25** and tricarbonyl(η-*exo*-*N*,2,5-trimethyl-1,2-dihydropyridine)chromium **26**. The part spectra could be assigned to **25** and **26** since the major component showed 2-H as a quartet, whereas the minor showed 6-H as a quintet due to accidental equivalence of the coupling to the methyl and 3-H.

This result is at first consideration rather unexpected, since to form the major complex **25** it is necessary to attack the pyridine ring at the more hindered 2-position. However, this is not the only factor to be considered. In many other reactions where the initial step is believed to be nucleophilic attack on a pyridine ring, *e.g.* the Chichibabin amination of pyridines, often a preference is taken for the more hindered site. For example, treatment of 3-methylpyridine **27** with sodamide in refluxing toluene gave predominantly the 2,3-isomer **28** as a 91:9 mixture with the 2,5-substituted product **29**.[10] Similarly, treatment of **27** with methyllithium afforded 2,3-lutidine **30** and the 2,5-isomer **31** in the ratio 84:16. This has been explained in the past as the result of weak London dispersion attractive forces between the 3-methyl group and the attacking nucleophile,[11] but probably a better explanation is that attack at the 2-position relieves steric compression between the 3-methyl group and hydrogens at the 2- and 4-position, whereas attack at the 6-position would only relieve the relatively mild steric compression between hydrogens at positions 4-, 5- and 6-. This can be illustrated in the case of

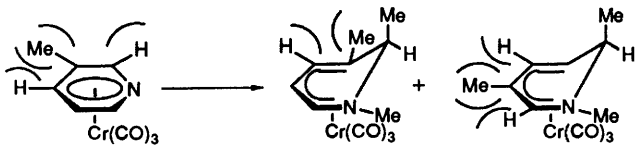


Fig. 1 Relief of steric compression on addition of methyllithium to complex **24**

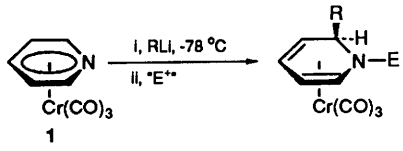
addition of methyllithium to complex **24** as shown in Fig. 1.

At first sight this may seem to preclude any regioselective addition to 3-substituted pyridine complexes, but this problem was overcome in the following way. Treatment of η-2-*tert*-butyldimethylsilyl-3-methylpyridine(tricarbonyl)chromium **32** with methyllithium followed by methyl iodide quench led to the formation of a single red compound identified as the product **33** of addition of methyllithium to the vacant 6-position in 95% yield. Complex **33** showed as well as the three ring protons, an *N*-methyl singlet at δ 2.68, a 9 H singlet at δ 1.11 along with two methyl singlets at 0.56 and 0.50 which showed that the *tert*-butyldimethylsilyl group had been retained. Also present was a single 3 H doublet at δ 0.63, derived from the *exo*-methyl group introduced by attack of the methyllithium. A molecular ion *m/z* 259 and correct elemental analysis confirmed the identity of **33**. Treatment of complex **33** with tetrabutylammonium fluoride in wet THF effected desilylation to give tricarbonyl(η-*exo*-*N*,2,5-trimethyl-1,2-dihydropyridine)chromium **26** in 98% yield whose ^{1}H NMR spectrum was identical with that of the minor component in the mixture obtained from addition of methyllithium to tricarbonyl(η-3-methylpyridine)chromium **24**. This pure regioisomer was fully characterised including elemental analysis. In an analogous manner, the other regioisomeric complex η-2-*tert*-butyldimethylsilyl-5-methylpyridine(tricarbonyl)chromium **34** was treated with methyllithium and the reaction mixture quenched with methyl iodide as before to afford the addition product **35** as red crystals in 96% yield. The ^{1}H NMR spectrum contained an *N*-methyl singlet at δ 2.64 along with a 9 H singlet at 1.07 and two 3 H singlets at 0.43 and 0.32, again showing that the *tert*-butyldimethylsilyl group had been retained. A doublet at δ 0.63 showed addition of the methyl group from methyllithium. This compound was fully characterised. Desilylation of **35** under the same conditions as for complex **33** led to a 97% yield of a compound whose ^{1}H NMR spectrum was identical with that of the major component of the mixture of products from addition of methyllithium to tricarbonyl(η-3-methylpyridine)chromium **24** and was assigned as tricarbonyl(η-*exo*-*N*,2,3-trimethyl-1,2-dihydropyridine)chromium **25**. This pure compound was then fully characterised, including elemental analysis (Scheme 4). The regiochemistry of the above additions follows unambiguously from the multiplicity of the methine proton in the ^{1}H NMR spectrum: a quartet for 2-H in **25** and a quartet for 2-H in **26**.

The scope of the addition of alkyllithiums to tricarbonyl(pyridine)chromium complexes appears to be quite general, both in the nature of the pyridine substrate and the alkyllithium itself. However, it was necessary to examine the generality of the electrophilic quench, in particular to see how much steric crowding could be tolerated around the nitrogen. Tricarbonyl(η-pyridine)chromium 1 was selected as substrate and methyllithium and *tert*-butyllithium chosen as representative nucleophiles. Addition of the alkyllithium to **1** was carried out in the normal way followed by addition of the electrophile and work-up. The results of these reactions are presented in Table 1.

From the results it appears that the reaction is general both in the trivial case of addition of a proton and in the nature of the alkyl halide. Yields were generally high for the cases where

Table 1 Addition of MeLi and Bu^{t}Li to complex **1** followed by various electrophilic quench

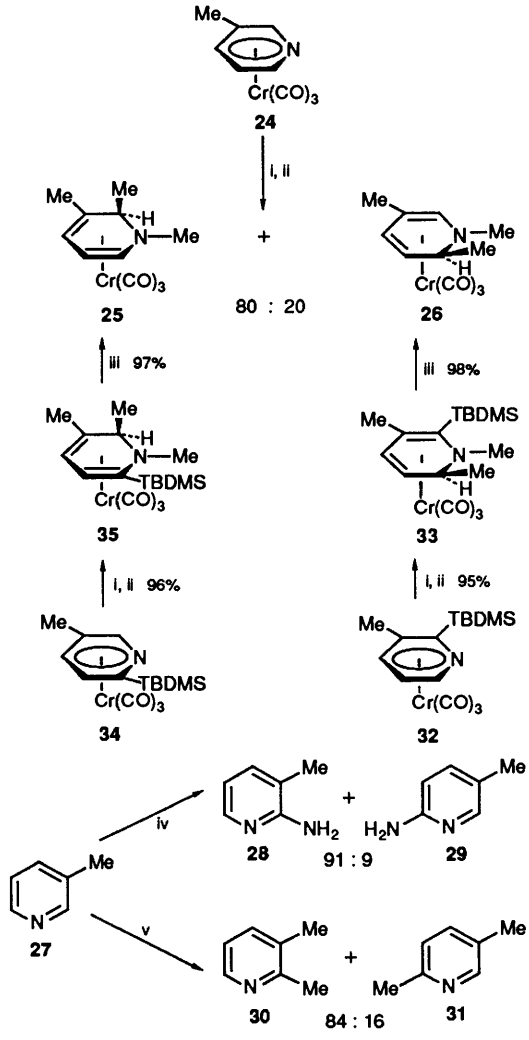


1

Entry	R	'E$^+$'	E	Product	Yield (%)
1	Me	MeOH	H–	**36**	100
2	Me	EtI	Et–	**37**	85
3	Me	BnBr	Bn–	**38**	100
4	Me	CH_2=$CHCH_2Br$	CH_2=CHMe	**39**	87
5	Me	CH_2=$CHCH_2CH_2Br$	CH_2=$CHCH_2Me$	**40**	95
6	Bu^t	MeOH	H–	**41**	86
7	Bu^t	EtI	Et–	**42**	62*
8	Bu^t	BnBr	Bn–	**43**	20†

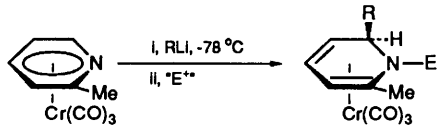
* 28% Of complex **41** isolated. † 60% Of complex **41** isolated.

methyllithium was used but for *tert*-butyllithium the reaction was not as successful. In the cases of entries 7 and 8 it was noted that as well as the relatively low yield of expected products **42** and **43**, the corresponding NH compound **41** was isolated. In the case of entry 7 this can be explained by the fact that since the resultant anion is somewhat sterically crowded it functions



Scheme 4 *Reagents:* i, MeLi, −78 °C; ii, MeI; iii, TBAF, H_2O; iv, $NaNH_2$, PhMe, heat; v, MeLi, heat

Table 2 Addition of MeLi and Bu^{t}Li to complex **14** followed by various electrophilic quench



14

Entry	R	'E$^+$'	E	Product	Yield (%)
1	Me	MeOH	H–	**44**	100
2	Me	EtI	Et–	**45**	90
3	Me	BnBr	Bn–	**46**	78
4	Me	CH_2=$CHCH_2Br$	CH_2=$CHCH_2Me$	**47**	60
5	Bu^t	MeOH	H–	**48**	95
6	Bu^t	EtI	Et–	**49**	62[a]
7	Bu^t	BnBr	Bn–	**50**	0[b]

[a] 25% Of complex **48** isolated. [b] 77% Of complex **48** isolated as only product.

as a base rather than a nucleophile, as evidenced by the rapid formation, on addition of ethyl iodide, of a red colour in the reaction mixture. With entry 8 (Table 1) the reaction is probably very slow, since prolonged reaction time did not produce the red colouration, the anion simply undergoing decomposition. Formation of **41** was due to quench by a proton source on work-up, *i.e.* from deactivated alumina.

In the light of the above reactions it was of interest to investigate the steric effect of the presence of a methyl group at the 6-position. The reactions were carried out in the same manner as those with **1**, the anion being generated from tricarbonyl(η-2-methylpyridine)chromium **14** and the appropriate electrophile being added after addition of the alkylithium. The results of these reactions are presented in Table 2. The reactions follow the same general pattern as those described for **1**. When methyllithium is employed as the nucleophile fair to excellent yields of the addition products are obtained, but on changing to *tert*-butyllithium the reaction becomes somewhat unfavourable, this being shown again for entries 6 and 7. In the case of entry 6 the isolation of complex **48** shows that the anion is functioning as a base, since on addition of ethyl iodide the solution became red in a short space of time. With entry 7 the only isolated product was complex **48** showing that the anion was too hindered to be quenched with benzyl bromide, since even on prolonged stirring no appreciable red colour developed and, in this instance, the anion is merely quenched with a proton source on work-up.

Conclusion

It has thus been shown that tricarbonyl(η-pyridine)chromium complexes undergo facile regio- and stereo-selective nucleophilic addition reactions with alkyllithium reagents to afford, on electrophilic quench, the corresponding tricarbonyl(η-*exo*-2-alkyl-1,2-dihydropyridine)chromium complexes in good to excellent yield. These latter complexes are useful stable, synthetic precursors to 1,2-dihydropyridines, the reactive free ligand can be liberated as required in the presence of appropriate trapping reagents.[12]

Experimental

General.—All reactions and purifications involving organometallic reagents were carried out under an atmosphere of nitrogen using vacuum line and Schlenk tube techniques[13] and all solvents were deoxygenated. For reactions with organic materials, no special conditions were used unless otherwise stated. All solvents were removed under reduced pressure. THF and ether were distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane was distilled from calcium hydride under nitrogen. Light petroleum refers to the fraction boiling in the range 40–60 °C and hexane in the range 67–70 °C. Tetrabutylammonium fluoride was Fluka purum grade. Butyllithium was used as a 1.4 mol dm^{-3} or 2.5 mol dm^{-3} solution in hexane, *tert*-butyllithium as a 1.7 mol dm^{-3} solution in pentane, methyllithium as a 1.0 mol dm^{-3} solution in ether and phenyllithium as a 2.0 mol dm^{-3} solution in cyclohexane. All other reagents were used as received or purified by standard methods.[14] Complexes **1**, **9**, **14**, **19**, **24**, **32** and **34** were prepared by previously described methods.[15]

^{1}H NMR spectra were recorded in deuteriochloroform on a Brüker WH 300 at 300.13 MHz and *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 by using electron impact or chemical ionisation techniques. Melting points were obtained on a Gallenkamp hot-stage melting point apparatus and are uncorrected. Elemental analyses were obtained by the Dyson Perrins analytical department.

Reduction of Tricarbonyl(pyridine)chromium **1**.—Tricarbonyl(pyridine)chromium 1 (90 mg, 0.418 mmol) was dissolved in toluene (15 ml) and cooled (−78 °C). DIBAL (0.4 ml, 0.48 mmol) was added, resulting in an instant colour change to red, and the mixture stirred (−78 °C; 2 h). Addition of methanol, warming (20 °C), and evaporation of solvent gave a red solid. Extraction (CH_2Cl_2; 15 ml) and filtration of the solution through alumina (CH_2Cl_2–methanol, 50:1) and evaporation afforded *tricarbonyl*(1,2-*dihydropyridine*)*chromium* **2** as a red microcrystalline solid (90 mg, 100%); m.p. 120 °C (decomp.); ν_{max}/cm^{-1} 3395 (NH), 1920, 1880, 1839 (CO); δ_H 5.92–5.82 (2 H, m, 3- and 5-H), 5.32 (1 H, t, *J* 6.7, 4-H), 3.75–3.66 (2 H, m, 2- and 6-H), 3.21 (1 H, d, *J* 10.3, 2-H), 2.30 (1 H, br s, N-H); *m*/*z* 217 (M$^+$) (Found: C, 44.0; H, 3.0; N, 6.15. $C_8H_7CrNO_3$ requires C, 44.25; H, 3.25; N, 6.45%).

General Procedure for Addition of Alkyllithiums to Tricarbonyl(pyridine)chromium Complexes.—A solution of the complex in THF (15 ml) at −78 °C was treated with *ca.* 1.1–1.2 equiv. of the relevant alkyllithium reagent and stirred (2–3 h) to give an orange solution. An excess of the electrophile was then added and the mixture allowed to warm to room temperature; stirring was then continued (24 h). Evaporation of solvent, extraction of the residue (2 × 10 ml; CH_2Cl_2) and evaporation of solvent left the crude addition product as a red solid. This was further purified by chromatography, using a light petroleum–ether solvent system as eluent, followed by recrystallisation where necessary, to afford the addition product as a red crystalline solid.

exo-2-*Butyl*-N-*methyl*-1,2-*dihydropyridine*(*tricarbonyl*)*chromium* **3**.—Tricarbonyl(pyridine)chromium 1 (100 mg, 0.465 mmol) was treated with butyllithium (0.4 ml, 0.56 mmol) and methyl iodide (0.2 ml, excess) according to the general procedure (eluent: 1:1) to give **3** as red blocks from isopentane (130 mg, 98%); m.p. 73 °C; ν_{max}/cm^{-1} 1950, 1870 and 1828 (CO); δ_H 5.72 (1 H, dt, *J* 1.5 and 5.0, 5-H), 5.36 (1 H, d, *J* 5.0, 6-H), 5.17 (1 H, dd, *J* 5.8 and 7.3, 4-H), 3.94 (1 H, ddd, *J* 0.6, 1.5 and 5.8, 3-H), 3.47 (1 H, m, 2-H), 2.58 (3 H, s, N-Me), 1.24–0.90 (6 H, m, $CH_2CH_2CH_2Me$) and 0.85 (3 H, t, *J* 7.0, $CH_2CH_2CH_2$*Me*); *m*/*z* 287 (M$^+$) (Found: C, 54.15; H, 6.0; N, 4.6. $C_{13}H_{17}CrNO_3$ requires C, 54.35; H, 6.0; N, 4.9%).

exo-2-*tert*-*Butyl*-N-*methyl*-1,2-*dihydropyridine*(*tricarbonyl*)*chromium* **5**.—Tricarbonyl(pyridine)chromium **1** (100 mg,

0.465 mmol) was treated with *tert*-butyllithium (0.35 ml, 0.6 mmol) and methyl iodide (0.2 ml, excess) according to the general procedure (eluent: 1:1) to give **5** as red blocks from isopentane (107 mg, 81%); m.p. 118 °C (decomp.); ν_{max}/cm^{-1} 1950, 1870 and 1827 (CO); δ_H 5.64–5.58 (2 H, m, 5- and 6-H), 5.26 (1 H, ddd, *J* 0.5, 1.3 and 2.0, 4-H), 3.83 (1 H, ddd, *J* 1.3, 2.0 and 6.5, 3-H), 3.33 (1 H, dd, *J* 1.3 and 5.3, 2-H), 2.79 (3 H, s, N-Me) and 0.76 (9 H, s, 2-Bu^t); *m/z* 287 (M^+) (Found: C, 54.0; H, 5.7; N, 5.15. $C_{13}H_{17}CrNO_3$ requires C, 54.35; H, 6.0; N, 4.9%).

Tricarbonyl(exo-N,2-*dimethyl*-1,2-*dihydropyridine*)*chromium* **6**.—Tricarbonyl(pyridine)chromium **1** (100 mg, 0.465 mmol) was treated with methyllithium (0.6 ml, 0.6 mmol) and methyl iodide (0.2 ml, excess) according to the general procedure (eluent: 2:3) to give **6** as red blocks from isopentane (108 mg, 95%); m.p. 93 °C; ν_{max}/cm^{-1} 1951, 1872 and 1840 (CO); δ_H 5.74 (1 H, dt, *J* 1.3 and 5.0, 5-H), 5.33 (1 H, d, *J* 5.0, 6-H), 5.17 (1 H, dd, *J* 5.0 and 5.5, 4-H), 3.92 (1 H, m, 3-H), 3.51 (1 H, q, *J* 6.3, 2-H), 2.55 (3 H, s, N-Me) and 0.62 (3 H, d, *J* 6.3, 2-Me); *m/z* 245 (M^+) (Found: C, 48.9; H, 4.6; N, 5.5. $C_{10}H_{11}CrNO_3$ requires C, 49.0; H, 4.5; N, 5.7%).

Tricarbonyl(N-*methyl*-exo-2-*phenyl*-1,2-*dihydropyridine*)-*chromium* **7**.—Tricarbonyl(pyridine)chromium **1** (100 mg, 0.465 mmol) was treated with phenyllithium (0.3 ml, 0.6 mmol) and methyl iodide (0.2 ml, excess) according to the standard procedure (eluent: 1:1) to give **7** as red needles from CH_2Cl_2–hexane (50 mg, 35%); m.p. 121 °C (decomp.); ν_{max}/cm^{-1} 1957, 1881 and 1845 (CO); δ_H 7.31–7.04 (5 H, m, Ph), 5.81 (1 H, dt, *J* 1.5 and 4.6, 5-H), 5.46 (1 H, dd, *J* 5.8 and 7.6, 3-H), 5.38 (1 H, d, *J* 4.6, 6-H), 4.45 (1 H, d, *J* 5.8, 2-H), 4.06 (1 H, dt, *J* 1.5 and 7.6, 4-H) at 2.58 (3 H, s, N-Me); *m/z* 307 (M^+) (Found: C, 58.4; H, 4.6; N, 4.3. $C_{15}H_{13}CrNO_3$ requires C, 58.6; H, 4.3; N, 4.6%).

exo-2-*Butyl*-6-tert-*butyldimethylsilyl*-N-*methyl*-1,2-*dihydropyridine*(*tricarbonyl*)*chromium* **10**.—2-*tert*-Butyldimethylsilylpyridine(tricarbonyl)chromium **9** (100 mg, 0.304 mmol) was treated with butyllithium (0.3 ml, 0.42 mmol) and methyl iodide (0.2 ml, excess) according to the standard procedure (eluent: 3:1) to give **10** as a deep red powder (120 mg, 99%); m.p. 99 °C; ν_{max}/cm^{-1} 1951, 1871 and 1836 (CO); δ_H 5.55 (1 H, dd, *J* 1.7 and 5.8, 5-H), 5.22 (1 H, dd, *J* 5.8 and 6.7, 4-H), 4.09 (1 H, ddd, *J* 1.7, 2.0 and 5.6, 3-H), 3.21 (1 H, m, 2-H), 2.64 (3 H, s, N-Me), 1.27–0.87 (6 H, m, $CH_2CH_2CH_2Me$), 1.06 (9 H, s, Bu^t), 0.83 (3 H, t, *J* 7.0, $CH_2CH_2CH_2Me$), 0.43 (3 H, s, Si-Me) and 0.32 (3 H, s, Si-Me); *m/z* 402 ($M^+ + 1$) (Found: C, 57.1; H, 8.1; N, 3.3. $C_{19}H_{31}CrNO_3Si$ requires C, 56.8; H, 7.8; N, 3.5%)

2-tert-*Butyl*-6-tert-*butyldimethylsilyl*-N-*methyl*-1,2-*dihydropyridine*(*tricarbonyl*)*chromium* **11**.—2-tert-Butyldimethylsilylpyridine(tricarbonyl)chromium **9** (100 mg, 0.304 mmol) was treated with *tert*-butyllithium (0.3 ml, 0.5 mmol) and methyl iodide (0.2 ml, excess) according to the standard procedure (eluent: 3:1) to give **11** as red needles from isopentane (97 mg, 80%); m.p. 137 °C; ν_{max}/cm^{-1} 1950, 1871 and 1836 (CO); δ_H 5.47 (1 H, dd, *J* 1.5 and 5.2, 5-H), 5.35 (1 H, m, 4-H), 4.00 (1 H, ddd, *J* 1.5, 2.0 and 5.2, 3-H), 3.26 (1 H, d, *J* 5.2, 2-H), 2.83 (3 H, s, N-Me), 1.11 (9 H, s, Si-Bu^t), 0.75 (9 H, s, 2-Bu^t), 0.46 (3 H, s, Si-Me) and 0.33 (3 H, s, Si-Me); *m/z* 401 (M^+) (Found: C, 56.5; H, 7.9; N, 3.3. $C_{19}H_{31}CrNO_3Si$ requires C, 56.8; H, 7.8; N, 3.5%).

6-tert-*Butyldimethylsilyl*-exo-N,2-*dimethyl*-1,2-*dihydropyridine*(*tricarbonyl*)*chromium* **12**.—2-*tert*-Butyldimethylsilylpyridine(tricarbonyl)chromium **9** (100 mg, 0.304 mmol) was treated with methyllithium (0.5 ml, 0.5 mmol) and methyl iodide (0.2 ml, excess) according to the standard procedure (eluent: 4:1) to give **12** as red blocks from isopentane (98 mg, 98%); m.p. 102 °C; ν_{max}/cm^{-1} 1950, 1872 and 1835 (CO); δ_H 5.57 (1 H, dd, *J* 1.6 and 5.8, 5-H), 5.24 (1 H, dd, *J* 5.8 and 7.7, 4-H), 4.06 (1 H, dt, *J* 1.6 and 7.7, 3-H), 3.41 (1 H, q, *J* 6.1, 2-H), 2.63 (3 H, s, N-Me), 1.07 (9 H, s, Si-Bu^t), 0.63 (3 H, d, *J* 6.1, 2-Me), 0.44 (3 H, s, Si-Me) and 0.33 (3 H, s, Si-Me); *m/z* 329 (M^+) (Found: C, 53.75; H, 7.2; N, 3.75. $C_{16}H_{25}CrNO_3Si$ requires C, 53.5; H, 7.0; N, 3.9%).

6-tert-*Butyldimethylsilyl*-N-*methyl*-exo-2-*phenyl*-1,2-*dihydropyridine*(*tricarbonyl*)*chromium* **13**.—2-*tert*-Butyldimethylsilylpyridine(tricarbonyl)chromium **9** (100 mg, 0.304 mmol) was treated with phenyllithium (0.25 ml, 0.5 mmol) and methyl iodide (0.2 ml, excess) according to procedure **B** (eluent: 3:1) to give **13** as red blocks from isopentane (119 mg, 93%); m.p. 122 °C (decomp.); ν_{max}/cm^{-1} 1945, 1869 and 1831 (CO); δ_H 7.30–7.09 (5 H, m, Ph), 5.70–5.60 (2 H, m, 4- and 5-H), 4.37 (1 H, d, *J* 5.5, 2-H), 4.06 (1 H, ddd, *J* 1.8, 2.0 and 7.7, 3-H), 2.71 (3 H, s, N-Me), 0.60 (9 H, s, SiBu^t), 0.32 (3 H, s, Si-Me) and 0.26 (3 H, s, Si-Me); *m/z* 329 (M^+) (Found: C, 59.8; H, 6.75; N, 3.1. $C_{21}H_{27}CrNO_3Si$ requires C, 59.8; H, 6.5; N, 3.3%).

exo-2-*Butyl*-N,6-*dimethyl*-1,2-*dihydropyridine*(*tricarbonyl*)-*chromium* **15**.—Tricarbonyl(2-methylpyridine)chromium **14** (100 mg, 0.437 mmol) was treated with butyllithium (0.4 ml, 0.56 mmol) and methyl iodide (0.2 ml, excess) according to the standard procedure (eluent: 3:1) to give **15** as red needles from CH_2Cl_2–hexane (50 mg, 35%); m.p. 96 °C; ν_{max}/cm^{-1} 1960, 1879 and 1842 (CO); δ_H 5.59 (1 H, d, *J* 5.5, 5-H), 5.09 (1 H, dd, *J* 5.5 and 7.4, 4-H), 3.87 (1 H, m, 3-H), 3.39 (1 H, m, 2-H), 2.69 (3 H, s, N-Me), 2.39 (3 H, s, 6-Me), 1.26–0.89 (6 H, m, $CH_2CH_2CH_2Me$) and 0.85 (3 H, t, *J* 7.0, $CH_2CH_2CH_2Me$); *m/z* 301 (M^+) (Found: C, 55.9; H, 6.4; N, 4.5. $C_{14}H_{19}CrNO_3$ requires C, 55.8; H, 6.4; N, 4.65%).

exo-2-tert-*Butyl*-N,6-*dimethyl*-1,2-*dihydropyridine*-(*tricarbonyl*)*chromium* **16**.—Tricarbonyl(2-methylpyridine)-chromium **14** (100 mg, 0.437 mmol) was treated with *tert*-butyllithium (0.3 ml, 0.5 mmol) and methyl iodide (0.2 ml, excess) according to the standard procedure (eluent: 3:1) to give **16** as orange–red needles from CH_2Cl_2–hexane (92 mg, 70%); m.p. 121 °C (decomp.); ν_{max}/cm^{-1} 1949, 1870 and 1834 (CO); δ_H 5.47 (1 H, d, *J* 5.5, 5-H), 5.18 (1 H, dd, *J* 5.7 and 7.1, 4-H), 3.78 (1 H, t, *J* 6.6, 3-H), 3.39 (1 H, d, *J* 5.7, 2-H), 2.88 (3 H, s, N-Me), 2.42 (3 H, s, 6-Me) and 0.78 (9 H, s, 2-Bu^t); *m/z* 301 (M^+) (Found: C, 55.7; H, 6.2; N, 4.5. $C_{14}H_{19}CrNO_3$ requires C, 55.8; H, 6.4; N, 4.65%).

Tricarbonyl(exo-N,2,6-*trimethyl*-1,2-*dihydropyridine*)-*chromium* **17**.—Tricarbonyl(2-methylpyridine)chromium **14** (100 mg, 0.437 mmol) was treated with methyllithium (0.5 ml, 0.5 mmol) and methyl iodide (0.2 ml, excess) according to the standard procedure (eluent: 2:1) to give **17** as deep orange blocks from CH_2Cl_2–hexane (91 mg, 80%); m.p. 128 °C (decomp.); ν_{max}/cm^{-1} 1951, 1872 and 1840 (CO); δ_H 5.61 (1 H, d, *J* 5.7, 5-H), 5.08 (1 H, dd, *J* 5.6 and 7.5, 4-H), 3.84 (1 H, m, 3-H), 3.55 (1 H, q, *J* 6.2, 2-H), 2.66 (3 H, s, N-Me), 2.35 (3 H, s, 6-Me) and 0.61 (3 H, d, *J* 6.2, 2-Me); *m/z* 259 (M^+) (Found: C, 50.7; H, 5.3; N, 5.1. $C_{11}H_{13}CrNO_3$ requires C, 51.0; H, 5.1; N, 5.4%).

Tricarbonyl(N,6-*dimethyl*-exo-2-*phenyl*-1,2-*dihydropyridine*)-*chromium* **18**.—Tricarbonyl(2-methylpyridine)chromium **14** (100 mg, 0.437 mmol) was treated with phenyllithium (0.25 ml, 0.5 mmol) and methyl iodide (0.2 ml, excess) according to the standard procedure (eluent: 2:1) to give **18** as red blocks from CH_2Cl_2–hexane (111 mg, 79%); m.p. 116 °C (decomp.); ν_{max}/cm^{-1} 1951, 1872 and 1840 (CO); δ_H 7.31–7.00 (5 H, m, Ph), 5.66 (1 H, d, *J* 5.6, 5-H), 5.34 (1 H, dd, *J* 5.6 and 7.6, 3-H), 4.51 (1 H, d, *J* 5.6, 2-H), 4.03 (1 H, m, 4-H), 2.70 (3 H, s, N-Me) and

2.32 (3 H, s, 6-Me); *m/z* 259 (M^+) (Found: C, 59.4; H, 4.5; N, 4.3. $C_{16}H_{15}CrNO_3$ requires C, 59.8; H, 4.7; N, 4.4%).

exo-2-*Butyl*-N,4-*dimethyl*-1,2-*dihydropyridine*(*tricarbonyl*)-*chromium* **20**.—Tricarbonyl(4-methylpyridine)chromium **19** (80 mg, 0.348 mmol) was treated with butyllithium (0.36 ml, 0.5 mmol) and methyl iodide (0.2 ml, excess) according to the standard procedure (eluent: 1:1) to give **20** as orange–red needles from isopentane (96 mg, 92%); m.p. 61 °C; ν_{max}/cm^{-1} 1964, 1881 and 1842 (CO); δ_H 5.58 (1 H, dd, *J* 2.0 and 4.7, 5-H), 5.36 (1 H, d, *J* 4.7, 6-H), 3.86 (1 H, dd, *J* 2.0 and 5.3, 3-H), 3.34 (1 H, m, 2-H), 2.56 (3 H, s, N-Me), 2.03 (3 H, s, 4-Me), 1.26–0.88 (6 H, m, $CH_2CH_2CH_2Me$) and 0.85 (3 H, t, *J* 6.9, $CH_2CH_2CH_2Me$); *m/z* 301 (M^+) (Found: C, 55.7; H, 6.45; N, 4.5. $C_{14}H_{19}CrNO_3$ requires C, 55.8; H, 6.4; N, 4.65%).

exo-2-tert-*Butyl*-N,4-*dimethyl*-1,2-*dihydropyridine*(*tricarbonyl*)chromium **21**.—Tricarbonyl(4-methylpyridine)chromium **18** (80 mg, 0.348 mmol) was treated with *tert*-butyllithium (0.3 ml, 0.5 mmol) and methyl iodide (0.2 ml, excess) according to the standard procedure (eluent: 3:1) to give **21** as orange–red needles from CH_2Cl_2–hexane (67 mg, 64%); m.p. 163 °C (decomp.); ν_{max}/cm^{-1} 1950, 1871 and 1837 (CO); δ_H 5.61 (1 H, d, *J* 3.6, 5-H), 5.50 (1 H, dd, *J* 2.0 and 3.6, 6-H), 3.76 (1 H, m, 3-H), 3.33 (1 H, d, *J* 5.1, 2-H), 2.79 (3 H, s, N-Me), 2.07 (3 H, s, 4-Me), 0.74 (9 H, s, Bu^t); *m/z* 301 (M^+) (Found: C, 56.0; H, 6.6; N, 4.5. $C_{14}H_{19}CrNO_3$ requires C, 55.8; H, 6.4; N, 4.65%).

Tricarbonyl(exo-N,2,4-*trimethyl*-1,2-*dihydropyridine*)-*chromium* **22**.—Tricarbonyl(4-methylpyridine)chromium **19** (80 mg, 0.348 mmol) was treated with methyllithium (0.5 ml, 0.5 mmol) and methyl iodide (0.2 ml, excess) according to the standard procedure (eluent: 2:3) to give **22** as orange–red needles from CH_2Cl_2–hexane (82 mg, 91%); m.p. 98 °C (decomp.); ν_{max}/cm^{-1} 1961, 1872, 1848 (CO); δ_H 5.60 (1 H, dd, *J* 1.7 and 4.7, 5-H), 5.34 (1 H, dd, *J* 1.7 and 4.7, 6-H), 3.84 (1 H, dd, *J* 1.7 and 5.3, 3-H), 3.50 (1 H, m, 2-H), 2.53 (3 H, s, N-Me), 2.01 (3 H, s, 4-Me) and 0.60 (3 H, d, *J* 6.3, 2-Me); *m/z* 259 (M^+) (Found: C, 50.8; H, 4.95; N, 5.1. $C_{11}H_{13}CrNO_3$ requires C, 51.0; H, 5.1; N, 5.4%).

Tricarbonyl(N,4-*dimethyl*-exo-2-*phenyl*-1,2-*dihydropyridine*)-*chromium* **23**.—Tricarbonyl(4-methylpyridine)chromium **19** (80 mg, 0.348 mmol) was treated with phenyllithium (0.25 ml, 0.5 mmol) and methyl iodide (0.2 ml, excess) according to the standard procedure (eluent: 1:2) to give **23** as red blocks from isopentane (48 mg, 43%); m.p. 114 °C (decomp.); ν_{max}/cm^{-1} 1965, 1890 and 1848 (CO); δ_H 7.30–7.01 (5 H, m, Ph), 5.67 (1 H, dd, *J* 1.9 and 4.9, 5-H), 5.38 (1 H, d, *J* 4.9, 6-H), 4.44 (1 H, d, *J* 5.4, 2-H), 3.99 (1 H, dd, *J* 1.9 and 5.4, 3-H), 2.57 (3 H, s, N-Me) and 2.16 (3 H, s, 4-Me); *m/z* 321 (M^+) (Found: C, 59.6; H, 4.8; N, 4.1. $C_{16}H_{15}CrNO_3$ requires C, 59.8; H, 4.7; N, 4.4%).

Addition of Methyllithium to Tricarbonyl(3-*methylpyridine*)-*chromium* **24** *with Methyl Iodide Quench*.—Tricarbonyl(3-methylpyridine)chromium **24** (80 mg, 0.348 mmol) was treated with methyllithium (0.5 ml, 0.5 mmol) and methyl iodide (0.2 ml, excess) according to the standard procedure to give a 80:20 mixture of *tricarbonyl*(exo-N,2,3-*trimethyl*-1,2-*dihydropyridine*)*chromium* **25** (eluent: 4:1) and *tricarbonyl*(exo-N,2,5-*trimethyl*-1,2-*dihydropyridine*)*chromium* **26** (eluent: 3:1). (For the characterisation data of these two compounds, see below.)

6-tert-*Butyldimethylsilyl*-exo-N,2,5-*trimethyl*-1,2-*dihydropyridine*(*tricarbonyl*)*chromium* **33**.—2-tert-*Butyldimethylsilyl*-3-*methylpyridine*(*tricarbonyl*)*chromium* **32** (70 mg, 0.204 mmol) was treated with methyllithium (0.3 ml, 0.3 mmol) and methyl iodide (0.2 ml, excess) according to the standard procedure (eluent: 5:1) to give **33** as red blocks from isopentane (72 mg, 95%); m.p. 115 °C; ν_{max}/cm^{-1} 1950, 1872 and 1834 (CO); δ_H 5.14 (1 H, d, *J* 7.9, 4-H), 4.19 (1 H, dd, *J* 6.0 and 7.9, 3-H), 3.30 (1 H, qu, *J* 6.0, 2-H), 2.68 (3 H, s, N-Me), 2.51 (3 H, s, 5-Me), 1.11 (9 H, s, Si-Bu^t), 0.63 (3 H, d, *J* 6.0, 2-Me), 0.56 (3 H, s, Si-Me) and 0.50 (3 H, s, Si-Me); *m/z* 373 (M^+) (Found: C, 54.55; H, 7.5; N, 4.1. $C_{17}H_{27}CrNO_3Si$ requires C, 54.7; H, 7.3; N, 3.75%).

Tricarbonyl(exo-N,2,5-*trimethyl*-1,2-*dihydropyridine*)-*chromium* **26**.—To 6-*tert*-butyldimethylsilyl-*exo*-*N*,2,5-trimethyl-1,2-dihydropyridine(tricarbonyl)chromium **33** (30 mg, 0.08 mmol) in THF (5 ml) was added tetrabutylammonium fluoride (50 mg, 0.158 mmol) and water (2 drops) at −78 °C; the solution was then stirred and allowed to warm to 20 °C with exclusion of light from the reaction mixture. After 1 h the resultant brown solution was evaporated and the residue IMMEDIATELY flash chromatographed (eluent: 3:1) to afford **26** as a red crystalline solid from CH_2Cl_2–hexane (20 mg, 98%); m.p. 136 °C (decomp.); ν_{max}/cm^{-1} 1960, 1879 and 1847 (CO); δ_H 5.24 (1 H, s, 6-H), 5.17 (1 H, d, *J* 7.9, 4-H), 3.94 (1 H, dd, *J* 7.9 and 6.3, 3-H), 3.44 (1 H, qu, *J* 6.3, 2-H), 2.50 (3 H, s, N-Me), 2.40 (3 H, s, 5-Me) and 0.60 (3 H, d, *J* 6.3, 2-Me); *m/z* 259 (M^+) (Found: C, 50.6; H, 5.1; N, 5.3. $C_{11}H_{13}CrNO_3$ requires C, 51.0; H, 5.1; N, 5.4%).

6-tert-*Butyldimethylsilyl*-exo-N,2,3-*trimethyl*-1,2-*dihydropyridine*(*tricarbonyl*)*chromium* **35**.—2-*tert*-Butyldimethylsilyl-5-methylpyridine(tricarbonyl)chromium **34** (70 mg, 0.204 mmol) was treated with methyllithium (0.3 ml, 0.3 mmol) and methyl iodide (0.2 ml, excess) according to the standard procedure (eluent: 3:1) to give **35** as red blocks from isopentane (73 mg, 96%); m.p. 140 °C; ν_{max}/cm^{-1} 1949, 1870 and 1832 (CO); δ_H 5.53 (1 H, d, *J* 5.8, 5-H), 4.99 (1 H, d, *J* 5.8, 4-H), 3.33 (1 H, q, *J* 6.4, 2-H), 2.64 (3 H, s, N-Me), 1.90 (3 H, s, 3-Me), 1.07 (9 H, s, SiBu^t), 0.63 (3 H, d, *J* 6.4, 2-Me), 0.43 (3 H, s, Si-Me) and 0.32 (3 H, s, Si-Me); *m/z* 373 (M^+) (Found: C, 54.65; H, 7.5; N, 3.3. $C_{17}H_{27}CrNO_3Si$ requires C, 54.7; H, 7.3; N, 3.75%).

Tricarbonyl(exo-N,2,3-*trimethyl*-1,2-*dihydropyridine*)-*chromium* **25**.—To 6-*tert*-Butyldimethylsilyl-*exo*-*N*,2,3-trimethyl-1,2-dihydropyridine(tricarbonyl)chromium **35** (30 mg, 0.08 mmol) in THF (5 ml) was added tetrabutylammonium fluoride (50 mg, 0.158 mmol) and water (2 drops) at −78 °C; the solution was then stirred and allowed to warm to 20 °C with exclusion of light from the reaction mixture. After 1 h the resultant brown solution was evaporated and the residue IMMEDIATELY flash chromatographed (eluent: 4:1) to afford **25** as a red crystalline solid from CH_2Cl_2–hexane (19 mg, 97%); m.p. 127 °C; ν_{max}/cm^{-1} 1969, 1883 and 1852 (CO); δ_H 5.68 (1 H, dd, *J* 4.7 and 5.8, 5-H), 5.27 (1 H, d, *J* 4.7, 6-H), 4.93 (1 H, d, *J* 5.8, 4-H), 3.43 (1 H, q, *J* 6.3, 2-H), 2.57 (3 H, s, N-Me), 2.40 (3 H, s, 3-Me) and 0.62 (3 H, d, *J* 6.3, 2-Me); *m/z* 259 (M^+) (Found: C, 50.7; H, 4.8; N, 5.6. $C_{11}H_{13}CrNO_3$ requires C, 51.0; H, 5.1; N, 5.4%).

Tricarbonyl(exo-2-*methyl*-1,2-*dihydropyridine*)*chromium* **36**.—Tricarbonyl(pyridine)chromium **1** (50 mg, 0.232 mmol) was treated with methyllithium (0.3 ml, 0.3 mmol) and methanol (0.2 ml, excess) according to the standard procedure (eluent: ether) to give **36** as red–orange crystals (53 mg, 100%); m.p. 109 °C (decomp.); ν_{max}/cm^{-1} 3400 (N-H), 1960, 1879 and 1842 (CO); δ_H 5.82 (1 H, t, *J* 5.0, 5-H), 5.68 (1 H, t, *J* 5.0, 6-H), 5.21 (1 H, m, 4-H), 4.02 (1 H, m, 3-H), 3.68 (1 H, m, 2-H), 2.77 (1 H, br s, N-H) and 0.68 (3 H, d, *J* 6.3, 2-Me); *m/z* 231 (M^+) (Found: C, 46.55; H, 3.8; N, 5.6. $C_9H_9CrNO_3$ requires C, 46.8; H, 3.9; N, 6.05%).

Tricarbonyl(N-*ethyl*-exo-2-*methyl*-1,2-*dihydropyridine*)-

chromium **37**.—Tricarbonyl(pyridine)chromium **1** (50 mg, 0.232 mmol) was treated with methyllithium (0.3 ml, 0.3 mmol) and ethyl iodide (0.2 ml, excess) according to the standard procedure (eluent: 3:2) to give **37** as red–orange flake crystals from CH_2Cl_2–hexane (51 mg, 85%); m.p. 95 °C (decomp.); ν_{max}/cm^{-1} 1960, 1883 and 1844 (CO); δ_H 5.74 (1 H, m, 5-H), 5.38 (1 H, d, *J* 4.8, 6-H), 5.18 (1 H, dd, *J* 5.7 and 7.3, 4-H), 3.82 (1 H, m, 3-H), 3.63 (1 H, qu, *J* 6.6, 2-H), 2.90 (1 H, m, N-CH_2CH$_3$), 2.35 (1 H, m, N-CH_2CH$_3$), 1.24 (3 H, t, *J* 7.2, N-CH$_2$CH_3), 0.63 (3 H, d, *J* 6.3, 2-Me); *m/z* 260 (M^+ + 1) (Found: C, 50.9; H, 4.9; N, 5.7. $C_{11}H_{13}CrNO_3$ requires C, 51.0; H, 5.05; N, 5.4%).

N-*Benzyl*-exo-2-*methyl*-1,2-*methyl*-1,2-*dihydropyridine*(*tricarbonyl*)*chromium* **38**.—Tricarbonyl(pyridine)chromium 1 (50 mg, 0.232 mmol) was treated with methyllithium (0.3 ml, 0.3 mmol) and benzyl bromide (0.15 ml, excess) according to the standard procedure (eluent: 2:3) to give **38** as red block crystals (74 mg, 100%); m.p. 107 °C; ν_{max}/cm^{-1} 1966, 1885 and 1841 (CO); δ_H 7.49–7.40 (5 H, m, Ph), 5.79 (1 H, m, 5-H), 5.55 (1 H, d, *J* 4.7, 6-H), 5.18 (1 H, dd, *J* 5.7 and 7.4, 4-H), 3.95, 3.38 (2 H, AB_{system}, J_{AB} 12.8, N-CH_2Ph), 3.72 (1 H, m, 3-H), 3.40 (1 H, qu, *J* 6.0, 2-H), 0.58 (3 H, d, *J* 6.3 Hz, 2-Me); *m/z* 322 (M^+ + 1) (Found: C, 59.8; H, 4.8; N, 4.2. $C_{16}H_{15}CrNO_3$ requires C, 59.8; H, 4.7; N, 4.4%).

N-*But*-3-*enyl*-exo-2-*methyl*-1,2-*dihydropyridine*(*tricarbonyl*)*chromium* **39**.—Pyridine(tricarbonyl)chromium **1** (100 mg, 0.465 mmol) was treated with methyllithium (0.6 ml, 0.6 mmol) and 1-bromobut-3-ene (0.3 ml, excess) according to the standard procedure (eluent: 1:1) to give **39** as red block crystals from CH_2Cl_2–hexane (115 mg, 87%); m.p. 60 °C; ν_{max}/cm^{-1} 1956, 1875 and 1840 (CO); δ_H 5.78–5.62 (2 H, m, 5-H and N-CH$_2$CH$_2$C*H*=CH$_2$), 5.40 (1 H, d, *J* 4.8, 6-H), 5.24 (3 H, m, 4- and N-CH$_2$CH$_2$CH=CH_2), 3.84 (1 H, dt, *J* 1.4 and 6.5, 3-H), 3.64 (1 H, qu, *J* 6.8, 2-H), 2.83 (1 H, m, N-CH_2CH$_2$CH=CH$_2$), 2.40 (3 H, m, N-CH_2CH_2CH=CH$_2$) and 0.65 (3 H, d, *J* 6.8, 2-Me); *m/z* 285 (M^+) (Found: C, 54.9; H, 5.4; N, 4.75. $C_{13}H_{15}CrNO_3$ requires C, 54.7; H, 5.3; N, 4.9%).

Tricarbonyl(exo-2-*methyl*-N-pent-4-enyl-1,2-*dihydropyridine*)*chromium* **40**.—Tricarbonyl(pyridine)chromium **1** (80 mg, 0.372 mmol) was treated with methyllithium (0.4 ml, 0.4 mmol) and 1-bromopent-4-ene (0.3 ml, excess) according to the standard procedure (eluent: 3:1) to give **40** as red block crystals from CH_2Cl_2–hexane (105 mg, 95%); m.p. 73 °C; ν_{max}/cm^{-1} 1954, 1873 and 1840 (CO); δ_H 5.84–5.71 (2 H, m, 5-H and N-CH$_2$CH$_2$CH$_2$C*H*=CH$_2$), 5.38 (1 H, d, *J* 4.8, 6-H), 5.20–5.03 (3 H, m, 4-H and N-CH$_2$CH$_2$CH$_2$CH=CH_2), 3.83 (1 H, m, 3-H), 3.62 (1 H, qu, *J* 6.8, 2-H), 2.74 (1 H, m, N-CH_2CH$_2$CH$_2$-CH=CH$_2$), 2.32 (1 H, m, N-CH_2CH$_2$CH$_2$CH=CH$_2$), 2.08 (2 H, m, N-CH$_2$CH$_2$CH_2CH=CH$_2$), 1.74 (2 H, m, N-CH$_2$CH_2CH$_2$-CH=CH$_2$) and 0.63 (3 H, d, *J* 6.8, 2-Me); *m/z* 299 (M^+) (Found: C, 56.5; H, 5.8; N, 4.6. $C_{14}H_{17}CrNO_3$ requires C, 56.2; H, 5.7; N, 4.7%).

exo-2-tert-*Butyl*-1,2-*dihydropyridine*(*tricarbonyl*)*chromium* **41**.—Tricarbonyl(pyridine)chromium **1** (50 mg, 0.232 mmol) was treated with *tert*-butyllithium (0.2 ml, 0.34 mmol) and methanol (0.2 ml, excess) according to the standard procedure eluent:ether) to give **41** as red–orange crystals (54 mg, 86%); m.p. 121 °C (decomp.); ν_{max}/cm^{-1} 3395 (NH), 1956, 1872 and 1836 (CO); δ_H 5.77–5.67 (2 H, m, 5- and 6-H), 5.21 (1 H, dd, *J* 5.6 and 8.0, 4-H), 3.97 (1 H, m, 3-H), 3.29 (1 H, t, *J* 4.4, 2-H), 2.86 (1 H, br s, NH), 0.68 (9 H, s, 2-Bu^t); *m/z* 273 (M^+) (Found: C, 52.6; H, 5.2; N, 4.8. $C_{12}H_{15}CrNO_3$ requires C, 52.75; H, 5.5; N, 5.1%).

exo-2-tert-*Butyl*-N-*ethyl*-1,2-*dihydropyridine*(*tricarbonyl*)*chromium* **42**.—Tricarbonyl(pyridine)chromium **1** (50 mg, 0.232 mmol) was treated with *tert*-butyllithium (0.2 ml, 0.34 mmol) and ethyl iodide (0.2 ml, excess) according to the standard procedure (eluent: 2:1) to give **42** as red–orange crystals (43 mg, 62%); m.p. 91 °C; ν_{max}/cm^{-1} 1961, 1879 and 1841 (CO); δ_H 5.63–5.57 (2 H, m, 5- and 6-H), 5.23 (1 H, dd, *J* 2.1 and 6.5, 4-H), 3.87 (1 H, dd, *J* 2.1 and 6.5, 3-H), 3.31 (1 H, d, *J* 5.2, 2-H), 2.88 (1 H, m, N-CH_2CH$_3$), 2.37 (1 H, m, N-CH_2CH$_3$), 1.26 (3 H, t, N-CH$_2$CH_3) and 0.73 (9 H, s, 2-Bu^t); *m/z* 302 (M^+ + 1) (Found: C, 55.5; H, 6.55; N, 4.5. $C_{14}H_{19}CrNO_3$ requires C, 55.8; H, 6.4; N, 4.65%).

Also recovered on further elution (ether) of the column was *exo*-2-*tert*-butyl-1,2-dihydropyridine(tricarbonyl)chromium **41** (17 mg, 28%), identical in all respects with the previously prepared sample.

N-*Benzyl*-exo-2-tert-*butyl*-1,2-*dihydropyridine*(*tricarbonyl*)*chromium* **43**.—Tricarbonyl(pyridine)chromium **1** (50 mg, 0.232 mmol) was treated with *tert*-butyllithium (0.2 ml, 0.34 mmol) and benzyl bromide (0.15 ml, excess) according to the standard procedure (eluent: 2:1) to give **43** as red needles from CH_2Cl_2–hexane (17 mg, 20%); m.p. 92 °C; ν_{max}/cm^{-1} 1953, 1871 and 1839 (CO); δ_H 7.53–7.47 (5 H, m, Ph), 5.65 (1 H, d, *J* 5.0, 5-H), 5.55 (1 H, m, 6-H), 5.27 (1 H, m, 4-H), 4.01, 3.79 (2 H, AB_{system}, J_{AB} 12.9, N-CH_2Ph), 3.60 (1 H, m, 3-H), 3.43 (1 H, d, *J* 6.6, 2-H), and 0.87 (9 H, s, 2-Bu^t); *m/z* 364 (M^+ + 1) (Found: C, 62.6; H, 5.9; N, 3.8. $C_{19}H_{21}CrNO_3$ requires C, 62.8; H, 5.8; N, 3.85%).

Also recovered on further elution (ether) of the column was *exo*-2-*tert*-butyl-1,2-dihydropyridine(tricarbonyl)chromium **41** (38 mg, 60%), identical in all respects with the previously prepared sample.

Tricarbonyl(exo-2,6-*dimethyl*-1,2-*dihydropyridine*)*chromium* **44**.—Tricarbonyl(2-methylpyridine)chromium **14** (50 mg, 0.218 mmol) was treated with methyllithium (0.25 ml, 0.25 mmol) and methanol (0.2 ml, excess) according to the standard procedure (eluent: ether) to give **44** as red–orange crystals (53 mg, 100%); m.p. 112 °C (decomp.); ν_{max}/cm^{-1} 3400 (NH), 1955, 1872 and 1831 (CO); δ_H 5.69 (1 H, d, *J* 5.6, 5-H), 5.14 (1 H, dd, *J* 5.6 and 7.7, 4-H), 3.92 (1 H, m, 3-H), 3.76 (1 H, m, 2-H), 2.79 (1 H, br s, N-H), 2.27 (3 H, s, 6-Me) and 0.69 (3 H, d, *J* 6.3, 2-Me); *m/z* 245 (M^+) (Found: C, 48.75; H, 4.7; N, 5.7. $C_{10}H_{11}CrNO_3$ requires C, 49.0; H, 4.5; N, 5.7%).

Tricarbonyl(N-*ethyl*-exo-2,6-*dimethyl*-1,2-*dihydropyridine*)*chromium* **45**.—Tricarbonyl(2-methylpyridine)chromium **14** (50 mg, 0.218 mmol) was treated with methyllithium (0.25 ml, 0.25 mmol) and ethyl iodide (0.2 ml, excess) according to the standard procedure (eluent: 3:1) to give **45** as red block crystals from CH_2Cl_2–hexane (54 mg, 90%); m.p. 132 °C (decomp.); ν_{max}/cm^{-1} 1950, 1870 and 1845 (CO); δ_H 5.63 (1 H, dd, *J* 1.3 and 5.5, 5-H), 5.10 (1 H, dd, *J* 5.5 and 7.7, 4-H), 3.81–3.70 (1 H, m, 2- and 3-H), 2.92 (1 H, m, N-CH_2CH$_3$), 2.73 (1 H, m, N-CH_2CH$_3$), 1.30 (3 H, t, *J* 7.2, N-CH$_2$CH_3) and 0.61 (3 H, d, *J* 6.2, 2-Me); *m/z* 273 (M^+) (Found: C, 52.7; H, 5.2; N, 4.8. $C_{12}H_{15}CrNO_3$ requires C, 52.75; H, 5.5; N, 5.1%).

N-*Benzyl*-exo-2,6-*dimethyl*-1,2-*dihydropyridine*(*tricarbonyl*)*chromium* **46**.—Tricarbonyl(2-methylpyridine)chromium **14** (50 mg, 0.218 mmol) was treated with methyllithium (0.25 ml, 0.25 mmol) and benzyl bromide (0.15 ml, excess) according to the standard procedure (eluent: 3:1) to give **46** as blood red block crystals (57 mg, 78%); m.p. 135 °C (decomp.); ν_{max}/cm^{-1} 1958, 1870 and 1839 (CO); δ_H 7.52–7.48 (5 H, m, Ph), 5.72 (1 H, dd, *J* 1.5 and 5.5, 5-H), 5.07 (1 H, dd, *J* 5.4 and 7.4, 4-H), 3.90, 3.72 (2 H, AB_{system}, J_{AB} 12.5, N-CH_2Ph), 3.61 (1 H, m, 3-H), 3.34 (1 H, qu, *J* 6.3, 2-H), 2.51 (3 H, s, 6-Me) and 0.60 (3 H, d, *J* 6.3,

2-Me); *m/z* 322 ($M^+ + 1$) (Found: C, 60.9; H, 5.2; N, 4.1. $C_{17}H_{17}CrNO_3$ requires C, 60.9; H, 5.1; N, 4.2%).

exo-2,6-*Dimethyl*-N-(1-*pent*-4-*enyl*)-1,2-*dihydropyridine*(*tricarbonyl*)*chromium* **48**.—Tricarbonyl(2-methylpyridine)chromium **14** (50 mg, 0.218 mmol) was treated with methyllithium (0.25 ml, 0.25 mmol) and 1-bromopent-4-ene (0.3 ml, excess) according to the standard procedure (eluent: 1:1) to give **47** as red block crystals from CH_2Cl_2–hexane (41 mg, 60%); m.p. 55 °C; ν_{max}/cm^{-1} 1955, 1873 and 1840 (CO); δ_H 5.79 (1 H, m, N-$CH_2CH_2CH_2CH$=CH_2), 5.62 (1 H, dd, *J*, 1.5 and 5.5, 5-H), 5.12–5.03 (3 H, m, 4-H and N-$CH_2CH_2CH_2CH$=CH_2), 3.79 (1 H, m, 3-H), 3.68 (1 H, qu, *J* 6.2, 2-H), 2.74 (2 H, m, N-$CH_2CH_2CH_2CH$=CH_2), 2.35 (3 H, s, 6-Me), 2.09 (2 H, m, N-$CH_2CH_2CH_2CH$=CH_2), 1.82 (2 H, m, N-$CH_2CH_2CH_2$-CH=CH_2) and 0.63 (3 H, d, *J* 6.2, 2-Me); *m/z* 313 (M^+) (Found: C, 57.6; H, 6.2; N, 4.4. $C_{15}H_{19}CrNO_3$ requires C, 57.5; H, 6.1; N, 4.5%).

exo-2-tert-*Butyl*-6-*methyl*-1,2-*dihydropyridine*(*tricarbonyl*)-*chromium* **48**.—Tricarbonyl(2-methylpyridine)chromium **14** (50 mg, 0.218 mmol) was treated with *tert*-butyllithium (0.15 ml, 0.255 mmol) and methanol (0.2 ml, excess) according to the standard procedure (eluent: ether) to give **48** as red blocks (60 mg, 95%); m.p. 116 °C (decomp.); ν_{max}/cm^{-1} 3395 (N-H), 1955, 1875 and 1841 (CO); δ_H 5.53 (1 H, d, *J* 5.6, 5-H), 5.26 (1 H, dd, *J* 5.7 and 7.9, 4-H), 3.91 (1 H, m, 3-H), 3.35 (1 H, m, 2-H), 2.95 (1 H, br s, N-H), 2.26 (3 H, s, 6-Me) and 0.67 (9 H, s, 2-Bu^t); *m/z* 287 (M^+) (Found: C, 54.6; H. 6.1; N, 5.0. $C_{13}H_{17}CrNO_3$ requires C, 54.35; H, 6.0; N, 4.9%).

exo-2-tert-*Butyl*-N-*ethyl*-6-*methyl*-1,2-*dihydropyridine*(*tricarbonyl*)*chromium* **49**.—Tricarbonyl(2-methylpyridine)chromium tricarbonyl **14** (50 mg, 0.218 mmol) was treated with *tert*-butyllithium (0.15 ml, 0.255 mmol) and ethyl iodide (0.2 ml, excess) according to the standard procedure (eluent: 4:1) to give **49** as red block crystals from heptane (43 mg, 62%); m.p. 118 °C; ν_{max}/cm^{-1} 1954, 1872 and 1840 (CO); δ_H 5.52 (1 H, dd, *J* 1.4 and 5.4, 5-H), 5.19 (1 H, dd, *J* 5.4 and 7.6, 4-H), 3.70 (1 H, m, 3-H), 3.56 (1 H, d, *J* 5.4, 2-H), 3.16 (1 H, m, N-CH_2CH_3), 2.74 (1 H, m, N-CH_2CH_3), 2.40 (3 H, s, 6-Me), 1.45 (3 H, t, *J* 7.0, N-CH_2CH_3) and 0.75 (9 H, s, 2-Bu^t); *m/z* 316 ($M^+ + 1$) (Found: C, 56.9; H, 6.95; N, 4.75. $C_{15}H_{21}CrNO_3$ requires C, 57.1; H, 6.7; N, 4.4%).

Also recovered on further elution (ether) of the column was complex *exo*-2-*tert*-butyl-6-methyl-1,2-dihydropyridine(tricarbonyl)chromium **48** (16 mg, 25%), identical in all respects with the previously prepared sample.

Reaction of Tricarbonyl(2-*methylpyridine*)*chromium* **14** *with* tert-*Butyllithium and Benzyl Bromide*.—Tricarbonyl(2-methylpyridine)chromium **14** (50 mg, 0.218 mmol) was treated with *tert*-butyllithium (0.15 ml, 0.255 mmol) and benzyl bromide (0.2 ml, excess) according to the standard procedure; the solution failed to lighten in colour. Work-up (eluent: ether) gave *exo*-2-*tert*-butyl-6-methyl-1,2-dihydropyridine(tricarbonyl)chromium **48** (48 mg, 77%) as the only isolable product, identical in all respects with the previously prepared sample.

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