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Chromium(0) tricarbonyl complexes of 1,3,5-triazacyclohexanes

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Three 1,3,5-trialkyl-1,3,5-triazacyclohexane chromium tricarbonyl complexes *fac*-[Cr(CO)$_3$(C$_3$H$_6$N$_3$R$_3$)] (R = Me, Et or Bu^t) have been prepared and their reactivities investigated. Both the kinetic and the thermodynamic stabilities of the complexes increase as the size of the R group increases. When R = Me or Et, the ligand is susceptible to displacement to produce [Cr(CO)$_3$L$_3$] [L = pyridine or P(OMe)$_3$]. Room-temperature single crystal X-ray studies were carried out on the R = Me and Bu^t complexes. Both molecules adopt the expected 'piano-stool' configuration with putative 3*m* symmetry; a crystallographic mirror plane passes through the methyl adduct. The Cr−N distances in the R = Me complex [2.153(3), 2 × 2.181(2) Å] are shorter than in the Bu^t case [2.202(5) − 2.216(4) Å]; in both the substituents are obligate equatorial relative to the triazacyclohexane ring.

The 1,3,5-trialkyl-1,3,5-triazacyclohexanes are a class of compounds which are readily accessible by the condensation of a primary amine with formaldehyde.[1] Despite the ease of preparation of triazacyclohexanes their co-ordination chemistry is only just beginning to be explored. Köhn and co-workers[2,3] recently prepared triazacyclohexane complexes of FeCl$_3$ and CrCl$_3$ by addition of the heterocycle to solutions of the metal halides. Prior to that work, Lüttringhaus and Kullick[4] had prepared some tricarbonyl complexes of Cr and Mo but these were only characterised by their infrared absorption spectra.

We have prepared a series of chromium tricarbonyl complexes (Scheme 1) of various triazacyclohexane derivatives in order to examine the influence of the alkyl substituents on the reactivity of these complexes. Crystal structure determinations for the trimethyl and tri-*tert*-butyl derivatives [Cr(CO)$_3$(tmtach)] and [Cr(CO)$_3$(tbtach)] are reported.

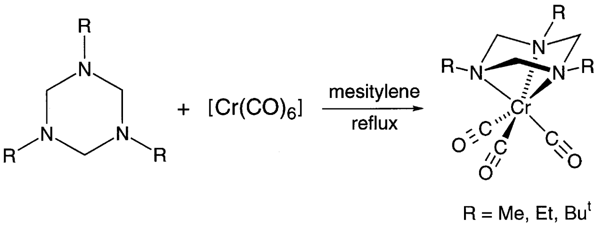
Results and Discussion

Synthesis of complexes and spectroscopic characterisation

The triazacyclohexane complexes were prepared in about 70% yield simply by heating the appropriate triazacyclohexane with [Cr(CO)$_6$] in mesitylene. The products precipitated from the reaction mixtures as orange solids and after isolation by filtration were sufficiently pure for most purposes. Although co-ordinating solvents such as tetrahydrofuran (thf) are commonly employed to promote the formation of other chromium tricarbonyl complexes, when used in the preparation of the present complexes these solvents were occluded within the solid product and could only be removed by recrystallisation.

The complexes were insoluble in non-polar organic solvents (*e.g.*, mesitylene, benzene) but dissolved sparingly in polar solvents {*e.g.*, solubility of [Cr(CO)$_3$(tmtach)] less than 0.4 mg cm^{-3} in thf, 19 mg cm^{-3} in Me$_2$SO} to form orange solutions. The solutions were air-sensitive and deposited green precipitates within a few minutes of exposure to the atmosphere. In the solid state the complexes were less air-sensitive: crystals of [Cr(CO)$_3$(tmtach)] and [Cr(CO)$_3$(tetach)] (R = Et) began to darken after 30 min of exposure to air and after 12 h were dark green, but [Cr(CO)$_3$(tbtach)] appeared to be stable indefinitely in air.

The spectroscopic properties of the complexes indicate that they are monomeric, with the heterocycle behaving as a tridentate ligand. Infrared spectra show two CO stretching bands, as expected for complexes containing a *fac*-Cr(CO)$_3$ group, and the frequencies of the CO stretches for [Cr(CO)$_3$(tmtach)] and [Cr(CO)$_3$(tetach)] match those reported previously.[4] The ^{1}H NMR spectra for the complexes contain two signals due to the methylene protons of the triazacyclohexane ring, one for the three axial protons and one for the three equatorial protons.



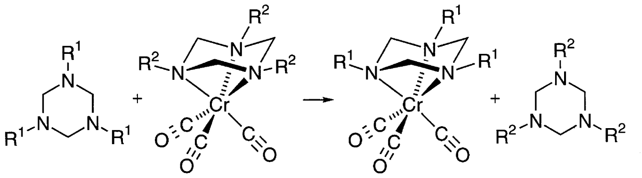
Scheme 1

Reactivity of the complexes

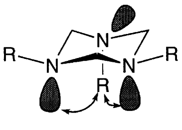
We investigated the reactivity of the complexes toward trimethyl phosphite to explore the lability of the heterocyclic ligands. When trimethyl phosphite was added to a solution of [Cr(CO)$_3$(tmtach)] in (CD$_3$)$_2$CO at room temperature, reaction occurred immediately, the tmtach ligand being displaced to produce *fac*-[Cr(CO)$_3${P(OMe)$_3$}$_3$]. Similar treatment of [Cr(CO)$_3$(tetach)] also produced *fac*-[Cr(CO)$_3${P(OMe)$_3$}$_3$], but the displacement of the tetach ligand occurred over several hours at room temperature. The [Cr(CO)$_3$(tbtach)] complex did not react, even after 1 week at room temperature. For the tetach and tbtach complexes, the amount of strain within the metal–ligand bonding is essentially the same as for the tmtach complex, so that the lower reactivity of the former may be attributed to a greater shielding of the metal from attack by trimethyl phosphite.

The substitution lability of the tmtach ligand is in stark contrast to the behaviour of the analogous triazacyclononane ligand 1,4,7-trimethyl-1,4,7-triazacyclononane (tmtacn) which is inert to displacement under a wide range of conditions.[5] This may be attributed to a combination of both a high degree of strain in the metal–tmtach bonding as well as greater accessibility of the metal to incoming ligands (due to the small 'cone angle' of tmtach compared to that of tmtacn).

A series of ligand-exchange experiments (Scheme 2) was carried out to explore the relative thermodynamic stabilities of the complexes. When approximately 1 equivalent of the R^1 heterocycle was added to a solution of the R^2 heterocyclic complex in (CD$_3$)$_2$CO at room temperature a ligand-exchange reaction



Scheme 2



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occurred to produce the R^1 heterocyclic complex and the free R^2 heterocycle, if R^1 was larger than R^2. This series of experiments shows that the thermodynamic stability of the complexes follows the order [Cr(CO)$_3$(tbtach)] > [Cr(CO)$_3$(tetach)] > [Cr(CO)$_3$(tmtach)].

The trend of increasing thermodynamic stability with increasing bulk of the R group in these complexes was surprising, since larger R groups might be expected to make binding of the chromium centre to the tertiary nitrogens more difficult. The trend in stability may be a reflection of the amount of strain in an uncomplexed triazacyclohexane in relation to the conformation that is imposed on the triazacyclohexane ring system by co-ordination to a Cr(CO)$_3$ unit. The preferred conformation for a free triazacyclohexane with aliphatic substituents is the *aee* conformation I, in which two of the R groups occupy equatorial positions and the remaining R group is in an axial position.[6,7] In this conformation the unfavourable steric interactions between the various R groups and the three nitrogen lone pairs are minimised. With aromatic (*p*-tolylmethyl and phenyl) substituents the *aae* array prevails in those examples so far structurally characterised.[8,9]

With increasing steric bulk of the R groups the unfavourable interactions between the axial R group and the two axial nitrogen lone pairs increases. The formation of the Cr(CO)$_3$ complex brings about a considerable relief of this steric and lone-pair repulsion, by allowing all of the R groups simultaneously to occupy equatorial sites. The larger the R group the larger is the relief of steric and lone-pair repulsion, and therefore the larger the thermodynamic gain, that occurs upon formation of the complex.

[Cr(CO)$_3$(tmtach)] as a source of Cr(CO)$_3$ in synthesis

The observation that displacement of tmtach from [Cr(CO)$_3$(tmtach)] occurs with such ease, with no requirement of heating, led us to explore the use of this complex as a source of the Cr(CO)$_3$ fragment. As mentioned above, the tmtach group was rapidly displaced by P(OMe)$_3$ in (CD$_3$)$_2$CO at room temperature. When less than 3 equivalents of P(OMe)$_3$ were used a mixture of *fac*-[Cr(CO)$_3${P(OMe)$_3$}$_3$] and [Cr(CO)$_3$(tmtach)] was obtained, no intermediate complexes being detected by ^{31}P or ^{1}H NMR spectroscopy. When ⩾3 equivalents of P(OMe)$_3$ were used *fac*-[Cr(CO)$_3${P(OMe)$_3$}$_3$] was formed quantitatively. Given the ease of preparation of [Cr(CO)$_3$(tmtach)], this reaction provides a more convenient route to *fac*-[Cr(CO)$_3${P(OMe)$_3$}$_3$] than the previously described syntheses starting with chromium tricarbonyl complexes of arenes or cycloheptatriene.[10]

The tmtach ligand was also displaced rapidly at room temperature by pyridine {to afford *fac*-[Cr(CO)$_3$(py)$_3$]} and by tributylphosphine {to afford *fac*-[Cr(CO)$_3$(PBu$_3$)$_3$]}. Tridentate tris(3,5-dimethylpyrazol-1-yl)methane, (dmpz)$_3$CH, displaced tmtach over a period of about 30 min in acetone solution at room temperature, to afford [Cr(CO)$_3${(dmpz)$_3$CH}]. In the latter reaction the product precipitated as a yellow solid which was identical to a sample prepared by heating a mixture of (dmpz)$_3$CH and [Cr(CO)$_6$] in dimethylformamide.[11]

We have not been able to use [Cr(CO)$_3$(tmtach)] as a starting material for the preparation of arenechromium tricarbonyl compounds. Indeed, tmtach appears to be an effective reagent for the displacement of the arene group from [Cr(CO)$_3$(arene)] complexes. For example, treatment of [Cr(CO)$_3$(C$_6$H$_5$OMe)] with tmtach in thf at reflux produced [Cr(CO)$_3$(tmtach)] and free anisole. This reaction illustrates a very mild method for removal of the Cr(CO)$_3$ group from [Cr(CO)$_3$(arene)] complexes compared to the commonly used methods such as heating in pyridine at reflux[12,13] or oxidative cleavage with I$_2$.[14] Since [Cr(CO)$_3$(tmtach)] is easily converted into [Cr(CO)$_3$(py)$_3$] and the latter can be used in a relatively mild (room-temperature) preparation of [Cr(CO)$_3$(arene)] complexes,[12] [Cr(CO)$_3$(tmtach)] may prove to be a useful intermediate in [Cr(CO)$_3$(arene)] chemistry.

Structural characterisation

The results of the room-temperature single crystal X-ray studies are consistent with the stoichiometry, connectivity and 'piano-stool' stereochemistry as implied above where R = Me or Bu^t. In the R = Bu^t adduct, one molecule, devoid of any crystallographically imposed symmetry, comprises the asymmetric unit of the structure; in the R = Me adduct, crystallising in a higher-symmetry array, we find the molecule disposed about a crystallographic mirror plane, with one half of it comprising the asymmetric unit. The molecules are depicted in Fig. 1, and their geometric parameters compared in Table 1. Both have putative 3*m* symmetry; the tach ring lies above the (CO)$_3$ array which is eclipsed by the ring carbon atoms, *i.e.* the substitutents are staggered in this projection. The Bu^t and Me arrays are likewise staggered about the N–C bond, the location of the methyl hydrogen atoms in the latter being established by refinement.

The chromium environments are closely similar in the two structures, although the Cr–N distances in the R = Me adduct, surprisingly disparate despite the higher intrinsic crystallographic symmetry of the array [2.153(3), 2.181(2) Å], are appreciably shorter than the much more closely ranged values of the thermodynamically more stable R = Bu^t complex. On the average, the C–Cr–C angles are smaller in the R = Bu^t adduct, although the diversity of values found in the R = Me adduct is such that attribution of significance to that observation is tenuous. Although the origin of the disparities in the R = Me adduct is presumably 'packing forces', the nature of these, presumably arising from (fairly numerous) CH $\cdots$ O contacts, is obscure. Suggestions that the longer Cr–N distances in the R = Bu^t adduct may be a consequence of steric strain are tenuously based also: contacts are found between carbonyl oxygen atoms and the substituent methyl groups which lie to either side at O $\cdots$ H distances of ≈2.6 Å, but there is little substantive evidence in other parameters of the system to support the notion that it is unduly sterically strained. Within [CrL$_3$(C$_3$H$_6$N$_3$R$_3$)] arrays the ring torsion angles are surprisingly uniform and insensitive to changes in R or L, lying close to 67° (Tables 1 and 2); in the variety of structural characterisations carried out on (non-disordered) free C$_3$H$_6$N$_3$R$_3$ of both *aee* and *aae* conformations, both compact and disparate ranges of ring torsion angles are found, but in all cases the mean of the distribution lies approximately 9° below the values found in the array of chromium complexes [*aee*: R = CH$_2$C(CH$_3$)$_3$, $|\tau| = 57.3(7)$–$62.0(9)°$;[6,7] R = cyclohexyl, $|\tau| = 55.8(2)$–$61.4(2)$;[15] *aae*: R = Ph, $|\tau| = 56._4$–$58._8°$;[9] R = *p*-tolylmethyl, $|\tau| = 50.6(2)$–$61.1(2)$[8]], *i.e.* about 58°. Thus, interestingly, the free C$_3$H$_6$N$_3$R$_3$ ring is 'flatter', *i.e.* less puckered, than the ring in its chromium complexes, a further factor in the balance of determinants of axial *vs.* equatorial substituent dispositions.

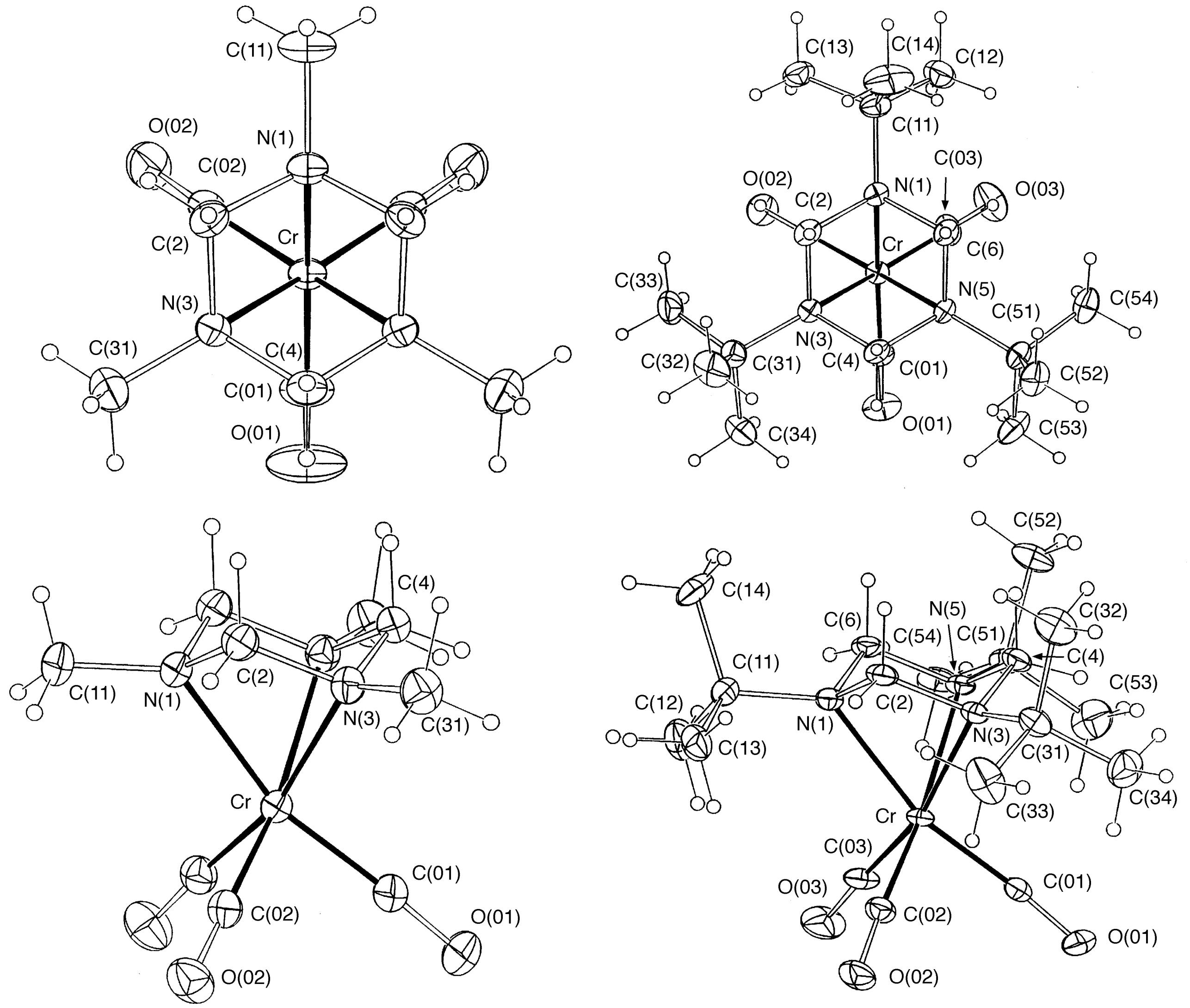

Fig. 1 Projections of [Cr(CO)$_3$(tmtach)] and [Cr(CO)$_3$(tbtach)] down and quasi-normal to the pseudo-three-fold axes of the molecules. 20% Thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å. For [Cr(CO)$_3$(tmtach)] a crystallographic mirror plane passes through N(1), Cr, C(4), and CO(01)

More far-ranging comparisons of interest about Cr as the central metal atom are possible with related systems, in which the carbonyl groups may be replaced by benzyl, in combination with bulky R = cyclohexyl, as in [Cr(CH$_2$Ph)$_3$(tctach)],[3] or by chloride, as in [CrCl$_3$(tnbtacn)] with the *n*-butyl-substituted tacn offering a different 'cone angle'.[16] Average values for these compounds in comparison with the present systems are given in Table 2. A feature worthy of note in this extended comparison, first of tach adducts, is the considerable lengthening of Cr–N with CH$_2$Ph replacing CO, presumably a consequence of diminished π bonding on the part of the unidentate ligand, and/or greater steric requirements of CH$_2$Ph *vs.* CO, as suggested by the considerable increase in C–Cr–C angles. With the tacn complex the Cr–N bond is diminished, in keeping with the increased N–Cr–N 'cone'; it is also of interest that, despite the diminished Cr–N, and despite the length of Cr–Cl, Cl–Cr–Cl is very large.

A further eighteen-electron [M(CO)$_3$(tacn)] system has been recorded for M = Re^{I},[17] while [Mn(CO)$_3$(NH$_3$)$_3$]$^+$ [as its Mn(CO)$_5^-$ salt][18] is relevant as a simple isoelectronic N$_3$M(CO)$_3$ system with unstrained N$_3$ array (of *m* symmetry). In the latter, Mn–N are 2.095(9), 2.097(5) (×2), Mn–C 1.774(7), 1.767(10) Å (×2), both appreciably shorter than the present, the Mn–N distance conspicuously so; N–Mn–N are 85.2(2), 86.6(2)° (×2), C–Mn–C 87.4(3) (×2), 91.1(3)°. The last angle is little changed from the present but the N–Mn–N are greatly expanded, with presumedly concomitant shortening of Mn–N.

Experimental

Nuclear magnetic resonance spectra were recorded using a Bruker ARX-500 spectrometer (500.1 for ^{1}H, 125.8 for ^{13}C and 202.5 MHz for ^{31}P) at ambient temperatures; ^{1}H and ^{13}C chemical shifts were referenced to solvent resonances, ^{31}P to external, neat 85% phosphoric acid (taken as δ 0.00). Infrared spectra were obtained using a Bio-Rad FTS-45 FTIR spectrophotometer, mass spectra using a VG Autospec mass spectrometer, fast atom bombardment (FAB) with a caesium-ion source and a *m*-nitrobenzyl alcohol matrix, or chemical ionisation with methane. Melting points were determined using an Electrothermal apparatus, with samples sealed in capillaries under nitrogen. Microanalyses were performed by CMAS, Belmont, Victoria, Australia. Manipulations involving chromium compounds were performed under nitrogen in Schlenk apparatus or in a dry-box. All solvents were distilled prior to use. Solvents used in the preparation or manipulation of air-sensitive compounds were dried, distilled and deoxygenated prior to use. Deoxygenation of solvents was carried out either by distillation under nitrogen or by at least three freeze–pump–thaw cycles. The tach compounds were prepared according to the method of Graymore.[1]

Synthesis of tricarbonyl(1,3,5-trialkyl-1,3,5-triazacyclohexane)chromium(0) complexes

[Cr(CO)$_3$(tmtach)]. A mixture of tmtach (1.0 g, 7.75 mmol)

Table 1 Selected molecular geometries for the compounds [Cr(CO)$_3$(tmtach)] and [Cr(CO)$_3$(tbtach)]

(*a*) Chromium environments (*r*/Å is the chromium–ligand atom distance; other entries in the matrices are the angles/° subtended at the relevant atoms at the head of the row and column)

(*i*) [Cr(CO)$_3$(tmtach)] (the square brackets indicate values that are redundant because there is a crystallographic mirror plane)

Atom	*r*	N(3)	N(3′)	C(01)	C(02)	C(02′)
N(1)	2.153(3)	63.46(8)	[63.46(8)]	164.2(2)	[102.5(1)]	102.5(1)
N(3)	2.181(2)		62.97(8)	103.4(1)	104.9(1)	164.1(1)
C(01)	1.791(4)				89.1(1)	[89.1(1)]
C(02)	1.804(3)					84.7(1)

(*ii*) [Cr(CO)$_3$(tbtach)]

Atom	*r*	N(3)	N(5)	C(02)	C(04)	C(06)
N(1)	2.216(4)	63.0(1)	63.4(2)	164.5(2)	105.9(2)	104.3(2)
N(3)	2.213(5)		63.4(2)	104.9(2)	105.2(2)	165.5(2)
N(5)	2.202(5)			103.2(2)	166.6(2)	105.3(2)
C(01)	1.785(5)				86.2(2)	86.1(2)
C(02)	1.799(6)					84.6(3)
C(03)	1.806(6)					

(*b*) Ligand geometries

[Cr(CO)$_3$(tmtach)]		[Cr(CO)$_3$(tbtach)]		[Cr(CO)$_3$(tmtach)]		[Cr(CO)$_3$(tbtach)]	
N(1)–C(2)	1.458(3)	N(1)–C(2)	1.470(7)	Cr–C(01)–O(01)	177.5(3)	Cr–C(01)–O(01)	175.9(5)
C(2)–N(3)	1.462(3)	N(1)–C(6)	1.473(7)	Cr–C(02)–O(02)	174.9(3)	Cr–C(02)–O(02)	176.0(5)
N(3)–C(4)	1.455(3)	C(2)–N(3)	1.459(6)			Cr–C(03)–O(03)	176.5(5)
		N(3)–C(4)	1.473(7)	Cr–N(1)–C(11)	129.6(3)	Cr–N(1)–C(11)	131.8(4)
		C(4)–N(5)	1.472(6)	Cr–N(3)–C(31)	133.5(2)	Cr–N(3)–C(31)	130.7(4)
		N(5)–C(6)	1.464(6)			Cr–N(5)–C(51)	131.7(4)
N(1)–C(11)	1.476(5)	N(1)–C(11)	1.513(6)	Cr–N(1)–C(2)	92.9(2)	Cr–N(1)–C(2,6)	92.2(3), 91.5(3)
N(3)–C(31)	1.468(4)	N(3)–C(31)	1.507(6)	Cr–N(3)–C(2)	91.7(2)	Cr–N(3)–C(2,4)	92.6(3), 91.9(3)
		N(5)–C(51)	1.501(7)	Cr–N(3)–C(4)	92.9(2)	Cr–N(5)–C(4,6)	92.4(3), 92.3(3)
C(01)–O(01)	1.178(5)	C(01)–O(01)	1.193(6)	N(1)–C(2)–N(3)	102.6(2)	N(1)–C(2)–N(3)	104.3(4)
C(02)–O(02)	1.167(3)	C(02)–O(02)	1.188(7)	N(3)–C(4)–N(3′)	103.0(3)	N(3)–C(4)–N(5)	103.9(4)
		C(03)–O(03)	1.171(8)			N(5)–C(6)–N(1)	104.3(4)

Ring torsion angles (atoms by number, *N* italicized)

tmtach		tbtach			
2′–*1*–2–*3*	−67.2(3)	6–*1*–2–*3*	−67.4(5)	*3*–4–*5*–6	67.5(5)
1–2–*3*–4	67.1(3)	*1*–2–*3*–4	67.9(5)	4–*5*–6–*1*	−67.3(5)
2–*3*–4–*3*	−67.5(3)	2–*3*–4–*5*	−67.8(5)	*5*–6–*1*–2	67.0(5)

and [Cr(CO)$_6$] (1.7 g, 7.75 mmol) was heated in mesitylene at reflux under nitrogen until the [Cr(CO)$_6$] no longer sublimed from the reaction mixture. During this time an orange precipitate was formed. The mixture was allowed to cool to room temperature and filtered, and the orange solid was washed with hexane to afford [Cr(CO)$_3$(tmtach)] as fine orange crystals (1.42 g, 69%), m.p. >240 °C (decomp.) (Found: C, 36.65; H, 5.05; N, 15.5. $C_9H_{15}CrN_3O_3$ requires C, 40.6; H, 6.05; N, 15.8%); $\tilde{\nu}_{max}$/cm^{-1} (Nujol) 1907, 1760 (CO) (lit.,[4] 1900, 1770); δ_H[(CD$_3$)$_2$CO] 2.49 (9 H, s, 3 × NCH$_3$), 4.02 (3 H, apparent d, splitting 8.3 Hz, 3 × NC*H*HN) and 4.66 (3 H, apparent d, splitting 8.3 Hz, 3 × NCH*H*N); δ_C[(CD$_3$)$_2$CO] 42.4 (CH$_3$), 83.2 (NCH$_2$N) and 237.5 (CO); *m*/*z* 266.0601 (*M* + H) (requires 266.0597).

The R = Et or Bu^t complexes were similarly prepared.

[Cr(CO)$_3$(tetach)]. Yield 68%; m.p. >250 °C (decomp.) (Found: C, 47.1; H, 7.0; N, 13.6. $C_{12}H_{21}CrN_3O_3$ requires C, 46.9; H, 6.9; N, 13.7%); $\tilde{\nu}_{max}$/cm^{-1} (Nujol) 1905, 1755 (CO) (lit.,[4] 1900, 1770); δ_H[(CD$_3$)$_2$CO] 1.26 (9 H, t, *J* 7.2, 3 × CH$_3$), 2.64 (6 H, q, *J* 7.2 Hz, 3 × C*H*$_2$CH$_3$), 4.01 (3 H, apparent d, splitting 8.3 Hz, 3 × NC*H*HN) and 4.64 (3 H, apparent d, splitting 8.3 Hz, 3 × NCH*H*N); δ_C[(CD$_3$)$_2$CO] 11.89 (CH$_3$), 48.88 (*C*H$_2$CH$_3$), 79.94 (NCH$_2$N) and 237.86 (CO); *m*/*z* 307.0963 (*M*) (requires 307.0988).

[Cr(CO)$_3$(tbtach)]. Yield 72%; m.p. >280 °C (decomp.) (Found: C, 55.25; H, 8.6; N, 10.75. $C_{18}H_{33}CrN_3O_3$ requires C, 55.2; H, 8.5; N, 10.75%); $\tilde{\nu}_{max}$/cm^{-1} (Nujol) 1901, 1765 (CO); δ_H[(CD$_3$)$_2$CO] 1.36 (27 H, s, 9 × CH$_3$), 4.06 (3 H, apparent d, splitting 8.7 Hz, NC*H*HN) and 5.16 (3 H, apparent d, splitting 8.7 Hz, NCH*H*N); δ_C[(CD$_3$)$_2$CO] 25.57 (CH$_3$), 56.98 [*C*(CH)$_3$], 73.32 (NCH$_2$N) and 237.54 (CO); *m*/*z* 391.1930 (*M*) (requires 391.1927).

Reaction of tmtach with [Cr(CO)$_3$(C$_6$H$_5$OMe)]

A solution of [Cr(CO)$_3$(C$_6$H$_5$OMe)] (100 mg, 0.41 mmol) and tmtach (0.1 cm^3, 0.71 mmol) in thf (20 cm^3) was heated at reflux for 24 h, resulting in the formation of an orange precipitate. The mixture was cooled to room temperature and the precipitate collected, washed with dry diethyl ether and dried under vacuum. This sample of [Cr(CO)$_3$(tmtach)] (77 mg, 71%) was identical to that prepared from tmtach and [Cr(CO)$_6$] as described earlier.

Reaction of [Cr(CO)$_3$(tmtach)] with pyridine

A small portion of [Cr(CO)$_3$(tmtach)] was dissolved in pyridine immediately giving a deep red solution. Addition of hexane afforded (quantitatively) deep red crystals of [Cr(CO)$_3$(py)$_3$], m.p. 74–76 °C (lit.,[19] 80 °C); $\tilde{\nu}_{max}$/cm^{-1} 1910 and 1778 (CO) (lit.,[20] 1908 and 1777).

Other displacements of tmtach from [Cr(CO)$_3$(tmtach)]

(*a*) By trimethyl phosphite. Trimethyl phosphite (0.9 mm^3, 7.5 μmol) was added *via* syringe to a solution of [Cr(CO)$_3$(tmtach)] (2 mg, 7.5 μmol) in (CD$_3$)$_2$CO (1 cm^3) in a 5 mm NMR tube fitted with a rubber septum. The solution changed

Table 2 Selected comparative mean geometries (distances in Å, angles in °)

	$[Cr(CO)_3(tmtach)]$	$[Cr(CO)_3(tbtach)]$	$[Cr(CH_2Ph)_3tctach)]$[3]	$[CrCl_3(tnbtacn)]$[16]
Cr−L[a]	1.800(7)	1.80(1)	2.122(4)	2.324(6)
Cr−N	2.17(2)	2.210(7)	2.28(1)	2.149(6)
N−C	1.458(2)	1.468(6)	1.476(8)	1.496(6)
N−C(*x*)	1.471(5)	1.507(6)	1.502(4)	1.503(3)
N−Cr−N	63.3(3)	63.3(2)	61.5(2)	82.4(4)
L−Cr−L	87(2)	85.6(9)	94(3)	92.4(7)
N−Cr−L(*trans*)	164.13(6)	165(1)	159(5)	173.0(9)
N−Cr−L	104(1)	104.8(9)	101(4)	92(1)
Cr−N−C(*x*)	132(2)	131.4(6)	134(2)	112(3)
Cr−N−C	92.8(5)	92.1(4)	92.5(7)	*b*
C−N−C	109.7(2)	108.0(1)	108.1(3)	110.8(5)
C−N−C(*x*)	113.3(7)	114.5(8)	113(2)	109.7(7)
Torsion angles (⟨|τ|⟩)				
C−N−C−N	67.2(3)	67.5(3)	67.0(9)	—

[a] L = Non-heterocyclic ligand. [b] Two sets of values: 109.1(4), 103.6(7)°.

immediately from orange to pale yellow. Analysis of the sample by ^{31}P and ^{1}H NMR spectroscopy indicated that *fac*-$[Cr(CO)_3\{P(OMe)_3\}_3]$ had been formed in quantitative yield. $\delta_H[(CD_3)_2CO]$ 3.64 (27 H, m, 9 × CH_3); $\delta_P[(CD_3)_2CO]$ 184.1 [lit.,[15] 186 (benzene)].

(***b***) **By tributylphosphine.** When the above experiment was repeated using tributylphosphine in place of trimethyl phosphite, the solution again changed immediately from orange to pale yellow. The product, formed in quantitative yield, was assigned as *fac*-$[Cr(CO)_3(PBu^n{}_3)_3]$ on the basis of its NMR spectra. $\delta_H[(CD_3)_2CO]$ 0.94 (27 H, t, *J* 7.4, $CH_3CH_2CH_2CH_2$), 1.41 (18 H, apparent sxt, *J* 7.4 Hz, $CH_3CH_2CH_2CH_2$), 1.58 (18 H, m, $CH_3CH_2CH_2CH_2$) and 1.79 (18 H, m, $CH_3CH_2CH_2CH_2$); $\delta_P[(CD_3)_2CO]$ 20.2.

(***c***) **By tris(3,5-dimethylpyrazol-1-yl)methane.** Tris(3,5-dimethylpyrazol-1-yl)methane (48 mg, 0.162 mmol) was added to a solution of $[Cr(CO)_3(tmtach)]$ (43 mg, 0.162 mmol) in acetone (30 cm^3). The solution changed from orange to yellow and a yellow solid precipitated. This solid was collected and washed with hexane to afford $[Cr(CO)_3\{(dmpz)_3CH\}]$ as a yellow powder (48 mg, 69%), m.p. >280 °C (decomp.); $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 1900, 1765 (CO) (lit.,[11] 1898, 1758); $\delta_H[(CD_3)_2CO]$ 2.01 (9 H, s, 3 × CH_3), 2.08 (9 H, s, 3 × CH_3), 6.06 (3 H, s, 3 × H^4) and 7.87 (1 H, s, methine HC); $\delta_C[(CD_3)_2CO]$ 10.33 (CH_3), 14.36 (CH_3), 107.38 (C^4), 140.96 (C^5), 153.86 (C^3) and 234.16 (CO); *m*/*z* 434.1181 (*M*) (requires 434.1158).

X-Ray crystallography

Crystals of $[Cr(CO)_3(tmtach)]$ and $[Cr(CO)_3(tbtach)]$ suitable for X-ray diffraction studies were grown from acetonitrile solutions.

Structure determinations. Unique room-temperature diffractometer data sets (2θ–θ scan mode; monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å) were measured yielding *N* independent reflections, N_o of these with $[I > 3\sigma(I)]$ being considered 'observed' and used in the full-matrix least-squares refinement after Gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atom; $(x, y, z, U_{iso})_H$ were refined for the methyl complex and constrained at estimated values for the *tert*-butyl complex. Conventional residuals *R*, *R′* on $|F|$ are quoted at convergence, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\ \sigma^4(I_{diff})$ being employed. Neutral atom complex scattering factors were used, the XTAL 3.2 program system being installed by S. R. Hall.[21]

Crystal/refinement data. $[Cr(CO)_3(tmtach)]$. $C_9H_{15}CrN_3O_3$, $M = 265.2$, orthorhombic, space group *Ibam* (D^{26}_{2h}, no. 72), $a = 14.537(5)$, $b = 13.953(3)$, $c = 12.757(3)$ Å, $U = 2587$ Å^3, D_c ($Z = 8$) = 1.36_2 g cm^{-3}, $F(000) = 1104$, $\mu_{Mo} = 8.8\ cm^{-1}$, specimen 0.20 × 0.55 × 0.35 mm, $A^*_{min,max} = 1.23, 1.40$, $2\theta_{max} = 70°$, $N = 2623$, $N_o = 1358$, $R = 0.042$, $R' = 0.045$.

$[Cr(CO)_3(tbtach)]$. $C_{18}H_{33}CrN_3O_3$, $M = 391.5$, monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), $a = 8.409(2)$, $b = 16.656(6)$, $c = 15.867(6)$ Å, $\beta = 110.36(3)°$, $U = 2085$ Å^3, D_c ($Z = 4$) = 1.24_7 g cm^{-3}, $F(000) = 840$, $\mu_{Mo} = 5.7\ cm^{-1}$, specimen 0.25 × 0.09 × 0.65 mm, $A^*_{min,max} = 1.06, 1.15$, $2\theta_{max} = 55°$, $N = 4767$, $N_o = 2670$, $R = 0.062$, $R' = 0.063$.

Abnormal features/variations in procedure. Crystals of the *tert*-butyl complex were micaceously twinned; after a number of attempts, a specimen was cleaved with a substantial dominant component, data being measured for that reciprocal lattice. Nevertheless, in the refinement it became evident that certain zones were affected by reflection superposition; these were treated with an independent scale factor. The experiment was repeated, but with a less congenial result; in the present report the rather high residual is ascribed to not-totally-satisfactory compensation for the effects of twinning, with a concomitant caveat concerning the possibility of systematic error in the details of the results.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/371.

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