Synthetic Applications of Tricarbonyl-η⁶-arenechromium(0) Complexes: The Synthesis of Benzo-fused Heterocycles

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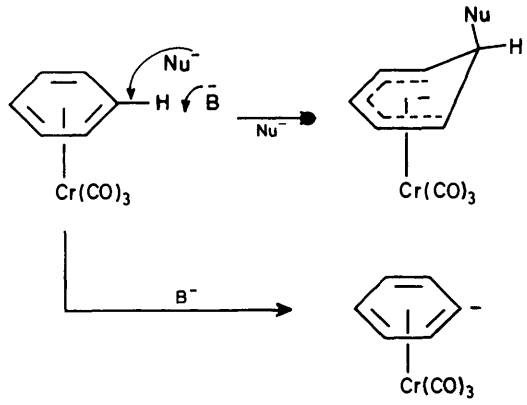
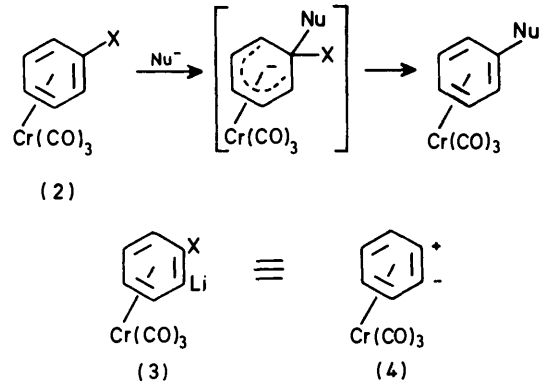
The reaction of tricarbonyl-η⁶-(2-fluorolithiobenzene)chromium(0) with bifunctional electrophiles produces a multistep cycloaddition reaction which generates 5-, 6-, or 7-membered benzo-fused heterocycles. The scope and limitations of the process are described.

The electronic effect of a tricarbonylchromium unit on the aromatic ring of a π-arene complex [as(1)] produces enhancement of the acidity of the aromatic protons and a susceptibility to nucleophilic attack on the ring (Scheme 1).[1] In particular, if a suitable leaving group is present [as (2)] then the overall reaction is one of nucleophilic aromatic substitution (Scheme 2).[2]

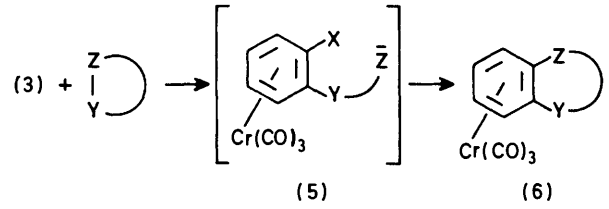


Scheme 1.



Scheme 2.

Since an electronegative group on an aromatic ring enhances the acidity of adjacent protons,[3] lithiation of a halogenobenzene complex would be expected to occur *ortho* to the halogen atom. Such a process has been shown to occur [4] but has, to date, been little exploited. The lithiated species is, in effect, a 1,2-dipolar synthon as depicted in (4), ostensibly analogous to a benzyne,† but strongly nucleophilic in character. Thus reaction with a potentially bifunctional electrophile (Scheme 3) can be envisaged in which the anionic component



Scheme 3.

liberated ($-Z^-$) is sufficiently nucleophilic to displace X^- and bring about a stepwise cycloaddition process under much milder conditions that have been achieved previously in unactivated systems.[5]

We now report a general study of this process as a means of forming benzo-heterocycles.

Initially, the choice of the group X in (3) was investigated. Tricarbonyl-η⁶-chlorobenzenechromium(0) (2; X = Cl) was produced in 96% yield from chlorobenzene and hexacarbonylchromium in 10% THF–dibutyl ether [6] using a Strohmeier apparatus.[7] Lithiation of (2; X = Cl) at −78 °C by addition to a solution of 1 equiv. of n-butyl-lithium in THF [4] gave predominantly the chlorobiaryl complex (7; X = Cl) which must arise as shown in Scheme 4. Metallation with t-butyl-lithium at −78 °C in THF and quenching the anion with ethyl chloroformate gave predominantly the complex of ethyl benzoate (8), with only minor amounts of ethyl 2-chlorobenzoate complex (9; X = Cl). The complex (8) presumably arose *via* a halogen-metal exchange lithiation. Surprisingly, no t-butyl addition to the ring was observed.[8] The chlorobenzene complex (2; X = Cl) is, therefore, not a suitable reagent for the cycloaddition reaction.

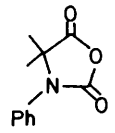
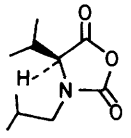
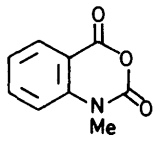
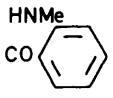
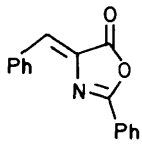
Tricarbonyl-η⁶-fluorobenzenechromium(0) (2; X = F), prepared analogously in 95% yield, was metallated by addition to a solution of t-butyl-lithium in THF at −78 °C in the presence of an excess of TMEDA. Reaction was complete within 5 min. The anion (3; X = F) was quenched with ethyl chloroformate, at −78 °C to give ethyl 2-fluorobenzoate complex (9; X = F) in 72% yield. Subsequent studies (see below) have shown that (3; X = F) is produced in >90% yield under these conditions. Again no t-butyl addition products were detected. The fluorobenzene complex is thus the reagent of choice.

With this established, we examined the scope of the initial

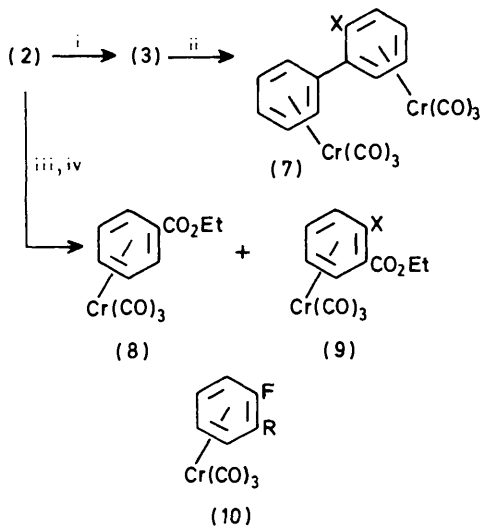
† We have no evidence to suggest that a benzyne complex is involved here.

Table 1. Electrophilic additions [a]

(3; X = F) + E ⟶ (10)

Run no.	E	Product (10; R =) [%]
1	PhNCO	CONHPh [80]
2	1-Naphthyl isocyanate	$CONHC_{10}H_7$ [56]
3	$Ph_2C{=}C{=}O$	$COCHPh_2$ [77]
4		$COCMe_2NHPh$ [61]
5		$COCHPr^iNHBu^i$ [37]
6		 [53]
7		-COC(NHCOPh)CHPh [73]

[a] All reactions used 1 equiv. of electrophile and were conducted at −78 °C.



Scheme 4. *Reagents and conditions:* i, Bu^nLi, THF, −78 °C; ii, (4; X = Cl); iii, Bu^tLi, THF, −78 °C; iv, $ClCO_2Et$

electrophilic addition to the anion (3; X = F). Firstly, the reaction with γ-butyrolactone was repeated under the reported conditions.[9] The tetrahydrobenzo-oxepinone complex (see Table 3, run 1) was isolated in 75% yield. A series of electrophiles was allowed to react with (3; X = F); those which added efficiently are given in Table 1.

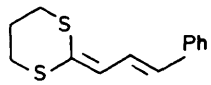
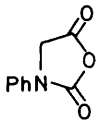
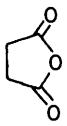
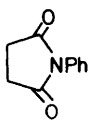
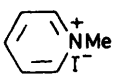
In assessing the scope of this reaction, a wide range of electrophiles were studied (Tables 1 and 2). It is evident that the high basicity of the complex is frequently dominant. This can be observed on addition of the substrate, in the immediate colour change (pale yellow to bright yellow) brought about by protonation, and the complete recovery of the starting complex (see Table 2, column i). The methylene dithianes normally undergo addition of unstabilised carbanions [10] but we observed only deprotonation. Although γ-butyrolactone added efficiently to (3; X = F), the remaining electrophiles of Table 2, column i, have only proton quenched material (2; X = F) despite their high electrophilicity.

Table 2, column ii contains two entries which gave, not the recovered starting complex, but the dimeric species (7; X = F) which presumably arises *via* a partial protonation of (3; X = F). Addition of the magnesium bromide [11] or lithium tetrachlorocuprate [12] to those reactions failed to effect alkylation. Certain species (Table 2, column iii) proved to be totally inert to the anion (3; X = F) which showed the relatively low nucleophilicity of this species.

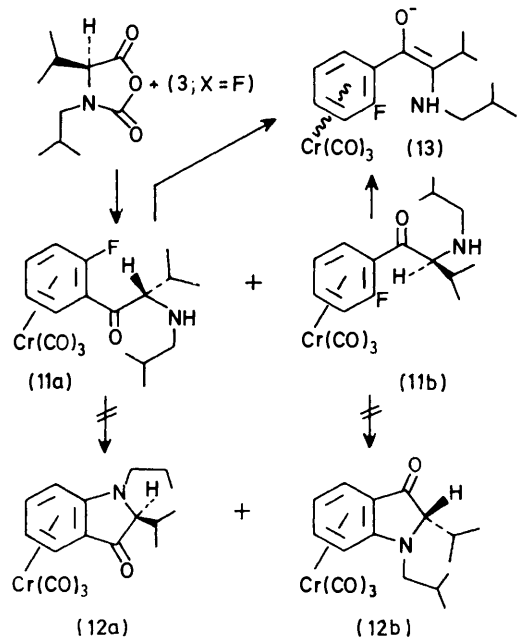
The substrates in Table 1, therefore all fall within the constraints of low (kinetic) acidity and high electrophilicity. The isocyanates and diphenylketene (Table 1, runs 1—3) reacted smoothly and efficiently. The anhydride and related systems (Table 1, runs 4,6,7) being devoid of acidic protons all acylated the anion in good yield. In each case, successful acylation was indicated by the deep red colour of the intermediate anion (5).

The chiral substrate, the *N*-carboxyanhydride of *N*-isobutyl-(*S*)-valine (Table 1, run 5), was studied in order to

Table 2. Electrophiles ineffective in the alkylation of (3; X = F)

i. Strong relative acidity [a]	ii. Weak relative acidity [a]	iii. Inert
		PhC≡CPh
		PhNSO
		PhCN
		
		
		
		
		

[a] We define these terms here by the behaviour of the electrophile towards (3; X = F). Strong relative acidity produced immediate proton quenching of the anion, weak relative acidity resulted in dimer (7; X = F) formation.



Scheme 5.

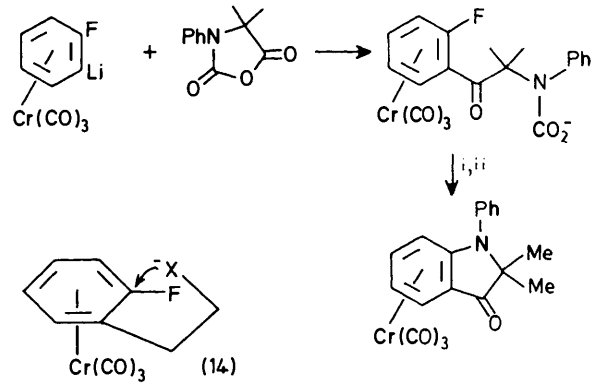
clarify two points. Firstly, could proton abstraction be inhibited by a sufficiently bulky blocking group and secondly, if the initial product cyclised, would there be dynamic stereoselection in the cyclisation step (Scheme 5)? Formation of (12b) would be expected to be inhibited by interaction between the isopropyl side chain and the chromium unit.

In the event, acylation of the anion to give (11a) and (11b) did occur in 37% yield, but no cyclisation (see below) was observed. This we attribute to preferential proton loss from the chiral carbon centre to give the anion (13). The potential for chiral synthesis inherent in the system is attractive and its development is in progress.

With the acylation of the anion (3; X = F) established we return to the original concept of one-pot cycloaddition reactions (Table 3). The butyrolactone result [9] indicated that a fused 7-membered ring was readily formed. Reaction of anion (3; X = F) with 2 equiv. of phenyl isocyanate at −78 °C, (Table 3, run 2) gave a rapid double addition and *in situ* cyclisation to produce the benzopyrimidinedione complex (Table 3, run 2) in 90% overall yield. The analogous di-1-naphthyl- (run 3) and diphenylbenzopyrimidine-dithione complexes (run 4) were formed in 61 and 65% yields respectively.

Some substrates which successfully acylated the anion would not cyclise (Table 1, runs 3, 5, 6, 7). Diphenylketene (run 3) gave the mono-addition product but no further reaction, even in the presence of an excess of ketene. The anhydride and azlactone substrates (runs 6, 7) failed to cyclise, apparently because of geometric constraints (see below).

The dimethyl-*N*-carboxyanhydride (Table 3, run 5) gave cyclised product after acid-catalysed decarboxylation (Scheme 6). Cyclisation would not proceed without prior formation of



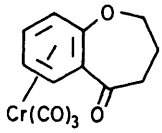
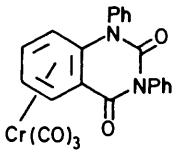
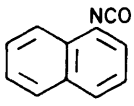
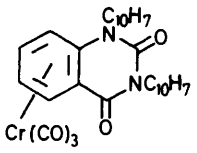
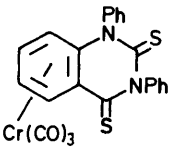
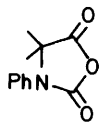
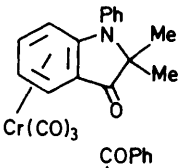
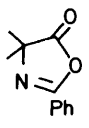
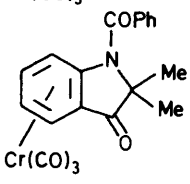
Scheme 6. *Reagents:* i, H^+; ii, LDA

the nitrogen anion. The dimethyl-azlactone (Table 3, run 6) gave a smooth, direct cycloaddition at −78 °C to the indoxyl complex in 75% yield. In contrast to our observations, is the reported failure [13] of the 2-fluoro-(2-hydroxyethyl)benzene complex (10; R = CH_2CH_2OH), where the nucleophile is oxygen, to cyclise under basic conditions.

The constraints so far revealed on the cyclisation process are (i) that the intermediate [as (1)] should have no sites of comparable acidity to the attacking heteroatom X-H and (ii) that for the formation of a 5-membered ring, there should be at least *one* sp^3 atom in the incipient ring in order to allow the correct geometry of approach to the aryl ring [as (14)], and (iii) that nitrogen is preferred to oxygen as the nucleophile for ring closure at least for the 5-membered rings.

Table 3. Cyclisation reactions

(3; X = F) + E ⟶ [(5)] ⟶ Product

Run no.	E	Equivalents	Product	(%)
1		1		(75)
2	PhNCO	2		(90)
3		2		(61)
4	PhNCS	4		(65)
5		1		(59)
6		1		(75)

Experimental

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected.

Analytical thin layer chromatography (t.l.c.) was performed on precoated silica GF_{254} plates. Column chromatography was carried out on silica gel 60H (Merck No. 7736). Samples were usually applied to the column pre-adsorbed onto a small amount of the appropriate silica.

All commercial reagents were purified according to standard techniques.[14] Solvents were purified as follows. Diethyl ether (ether) and tetrahydrofuran (THF) were freshly distilled from NaK alloy and benzophenone ketyl under nitrogen. Di-n-butyl ether was dried by storage over sodium wire and distillation from sodium, under nitrogen, prior to use. Light petroleum (b.p. 40—60 °C) (petroleum) for column chromatography was redistilled before use.

The tricarbonylchromium(0) complexes were prepared using a Strohmeier apparatus [7] without cooling water in the jackets. Under these conditions very high yields of complexes could be routinely produced without the inconvenience of the constant temperature water supplies originally described.

Tricarbonyl-η⁶-chlorobenzenechromium(0) (2; R = Cl).—A deoxygenated mixture of di-n-butyl ether (80 ml), THF (8 ml), chlorobenzene (10 ml), and hexacarbonylchromium (1.0 g) was refluxed for 24 h under nitrogen. After cooling, the bright yellow solution was diluted with ether and filtered through a short column of silica. Evaporation of the solvent (80—100 °C) gave (2; R = Cl) (1.08 g, 96%) as a yellow crystalline solid, m.p. 99—100 °C (lit.,[2,6] m.p. 102—103 °C); $\nu_{max.}$ (Nujol) 3 100, 1 955, 1 880, 810, 700, 660, and 625 cm^{-1}; δ($CDCl_3$) 4.8—5.2 (1 H, m) and 5.2—5.7 (4 H, m); *m/z* 248 (M^+), 220, 192, 164, 112, and 52.

Tricarbonyl-η⁶-fluorobenzenechromium(0) (2; R = F).—The reaction was carried out as above using fluorobenzene (10 ml) and refluxing for 48 h. The fluorobenzene complex (2; R = F) (1.0 g, 95%)was isolated as a yellow crystalline solid, m.p. 100—101 °C (lit.,[2,6] m.p. 107 °C); $\nu_{max.}$ (Nujol) 3 090, 1 980, 1 960, 1 615, 1 870, 810, 795, 665, 650, and 630 cm^{-1}; δ($CDCl_3$) 4.6—5.0 (1 H, m), and 5.0—5.7 (4 H, m); *m/z* 232 (M^+), 204, 176, 148, 96, and 52.

Tricarbonyl-η⁶-2-ethoxycarbonylfluorobenzenechromium(0) (9; X = F).—A deoxygenated mixture of di-n-butyl ether (30 ml), THF (10 ml), ethyl 2-fluorobenzoate (400 mg, 2.4 mmol), and hexacarbonylchromium (500 mg, 2.2 mmol) was refluxed for 18 h under dry nitrogen. The resulting solution was diluted with ether, filtered through a short column of silica, and the solvent evaporated. Purification by column chromatography (ether–petroleum) gave the product (9; X = F) (302 mg, 42%) as an orange oil, identical in all respect with the sample obtained below.

Lithiation of Tricarbonyl-η⁶-chlorobenzenechromium(0).—(i) *With n-butyl-lithium.* A solution of the chlorobenzene complex (2; X = Cl) (145 mg, 0.58 mmol) in THF (15 ml) was treated with Bu^{n}Li (0.6 mmol, 1 equiv.) at −78 °C. After 4 h the reaction was warmed to room temperature and quenched with dilute hydrochloric acid. Extraction with ether followed by drying (K_2CO_3) and evaporation of solvent gave a dark yellow oil which was subjected to column chromatography (ether–petroleum). The product, 2-chlorobiphenylbis[tricarbonylchromium(0)] (7; X = Cl) (25 mg, 19%) was isolated as a yellow crystalline solid, m.p. 127—128 °C (from cyclohexane); $\nu_{max.}$ (Nujol) 1 965, 1 900, 1 875, 655, and 625 cm^{-1}; δ_H($CDCl_3$) 4.9—5.9, (m); δ_C($CDCl_3$) 81.51 (s), 82.51 (s), 82.71 (s), 82.91 (s), 85.31 (s), 85.71 (s), 86.91 (s), and 87.51 (s); *m/z* 460 (M^+), 376, 320, 292, 240, and 205 (Found: C, 46.65; H, 2.05; Cl, 7.75. $C_{18}H_9ClCr_2O_6$ requires C, 46.92; H, 1.97; Cl, 7.69%).

(ii) *With t-butyl-lithium.* To a solution of Bu^{t}Li (1.05 mmol) in THF (20 ml) at −78 °C was added a solution of chlorobenzene (230 mg, 0.92 mmol) in THF (5 ml). After 15 min, an excess of ethyl chloroformate (3 ml) was added, and, after a further 30 min, at −78 °C, the reaction was allowed to warm to room temperature. Addition of water, ether extraction, drying (K_2CO_3), and evaporation of solvents gave a red oil which on column chromatography (ether–petroleum) gave an orange oil (200 mg) which had a mass spectrum consistent with a mixture of chloro ester (9; X = Cl) (M^+, 320) (minor) and ethyl benzoate complex (2; X = CO_2Et) (M^+, 286) (major).

General Procedure for the Preparation of Tricarbonyl-η⁶-(2-fluorolithiobenzene)chromium(0) (3; X = F) *and its Reaction with Electrophiles.*—To a solution of t-butyl-lithium (1.05 mmol) in THF (70 ml) and TMEDA (2 ml), maintained under dry nitrogen at −78 °C, was added a solution of the fluorobenzene complex (2; X = F) (232 mg, 1 mmol) in THF (10 ml). After 30 min the product, tricarbonyl-η⁶-(2-fluorolithiobenzene)chromium(0) (3; X = F) was treated with a solution of the electrophile in THF (10 ml) and allowed to react at −78 °C for 2 h, at −20 °C for a further 2 h, and finally at room temperature for a further 16 h. Work-up with dilute hydrochloric acid and extraction with ether, after drying (K_2CO_3) and evaporation of solvent, gave an oil which was subjected to column chromatography (ether–petroleum).

All complexes were crystallised by addition of light petroleum to a concentrated chloroform solution of the complex under nitrogen with protection from light.

Reactions of the Lithiated Complex (3; X = F) *with Electrophiles.—Ethyl chloroformate.* The reaction was carried out according to the general procedure with an excess of ethyl chloroformate (1 ml) as the electrophile. The product complex (9; X = F) (219 mg, 72%) was isolated as an orange oil; $\nu_{max.}$ (neat) 3 100, 2 980, 1 975, 1 900, 1 720, 660, 645, and 610 cm^{-1}; δ_H($CDCl_3$) 1.38 (3 H, t, *J* 7 Hz), 4.35 (2 H, q, *J* 7 Hz), 4.7—5.1 (1 H, m), 5.2—5.5 (1 H, m), 5.5—5.8 (1 H, m), and 6.0—6.3 (1 H, m); *m/z* 304 (M^+), 248, 220, and 192 (Found: *M*, *m/z* 303.9838. $C_{12}H_9CrFO_5$ requires *M* 303.9839).

γ-Butyrolactone. The general procedure was carried out using γ-butyrolactone (95 mg, 1.1 equiv.) as the electrophile. The product, tricarbonyl-η⁶-(4,5,6,7-tetrahydrobenzo[*b*]oxepin-4-one)chromium(0),* (223 mg, 75%) was isolated as an orange oil which solidified with time but could not be crystallised; $\nu_{max.}$ (neat) 1 960, 1 885, 1 675, 670, 650, and 615 cm^{-1}; δ($CDCl_3$) 1.75—2.55 (2 H, m), 2.60—3.20 (2 H, m), 3.80—4.70 (2 H, m), 4.82—5.05 (1 H, m), 5.12—5.30 (1 H, m), 5.52—5.75 (1 H, m), and 5.95—6.10 (1 H, m); *m/z* 298 (M^+), 242, 214, and 105 (Found: *M*, *m/z* 297.9939. $C_{13}H_{10}CrO_5$ requires *M*, 297.9933.

Phenyl isocyanate (1 *equiv.*). The general procedure was carried out with phenyl isocyanate (119 mg, 1 mmol) as the electrophile. The major product (10; R = CONHPh) (280 mg, 80%) was isolated as an orange crystalline solid, m.p. 126.5—128 °C (decomp.); $\nu_{max.}$ (Nujol) 3 300, 1 970, 1900, 1 875, 1 655, 755, and 685 cm^{-1}; δ-($CDCl_3$) 4.1—5.1 (3 H, m), 5.5—5.8 (1 H, m), and 7.2—8.3 (5 H, m); *m/z* 351 (M^+), 295, and 267 (Found: C, 54.5; H, 2.9; N, 3.95. $C_{16}H_{10}CrFNO_4$ requires C, 54.71; H, 2.87; N, 3.99%).

Further elution with ether–petroleum (1 : 1) gave the minor product tricarbonyl-η⁶-(1,3-diphenylquinazoline-2,4-dione)-chromium(0) (25 mg, 5%) as an orange crystalline solid, m.p. 119—120 °C (decomp.) identical with the sample prepared below.

Phenylisocyanate (2 *equiv.*). The reaction was carried out according to the general procedure using phenyl isocyanate (238 mg, 2 mmol) as the electrophile. The product tricarbonyl-η⁶-(1,3-diphenylquinozoline-2,4-dione)chromium(0) (410 mg, 90%) was isolated as an orange crystalline solid, m.p. 119—120 °C (decomp.); $\nu_{max.}$ (Nujol) 1 965, 1 870, 1 715, 1 670, 690, 645, and 610 cm^{-1}; δ_H($CDCl_3$), 4.6—4.8 (1 H, m), 4.9—5.2 (1 H, m), 5.5—5.8 (1 H, m), 6.4—6.7 (1 H, m), and 7.2—7.8 (10 H, m); *m/z* 450 (M^+), 366, and 314 (Found: C, 61.15; H, 3.2; N, 6.05. $C_{23}H_{14}CrN_2O_5$ requires C, 61.34; H, 3.13; N, 6.22%).

A sample of this complex (400 mg, 0.89 mmol) was decomplexed by treatment with iodine (400 mg, 1.2 equiv.) in chloroform (10 ml) for 24 h at room temperature. After the reaction mixture had been washed with aqueous sodium bisuphite solution and water, the organic solution was dried (K_2CO_3) and the solvent removed. Column chromatography (ether–petroleum) gave 1,3-diphenylquinazoline-2,4-dione as a white crystalline solid, m.p. 176—177 °C (from ethanol). (Found: C, 76.2; H, 4.25; N, 8.9. $C_{20}H_{14}N_2O_2$ requires C, 76.43; H, 4.46; N, 8.92%).

1-*Naphthyl isocyanate* (1 *equiv.*). The general procedure was repeated using 1-naphthyl isocyanate (169 mg, 1 mmol) as the electrophile. The product (10; R = $CONHC_{10}H_7$) (223 mg, 56%) was obtained as dark orange crystals, m.p. 149—150 °C; $\nu_{max.}$ (Nujol) 3 200—3 480, 1 975, 1 900, 1 660, 790, 765, 750, 660, 650, and 620 cm^{-1}; δ_H($CDCl_3$) 4.5—6.5 (4 H, m) and 7.0—8.5 (7 H, m); *m/z* 401 (M^+), 345, 317, and 265 (Found: C, 60.15; H, 3.05; N, 3.6. $C_{20}H_{12}CrFNO_4$ requires C, 59.68; H, 3.01; N, 3.49%).

1-*Naphthyl isocyanate* (2 *equiv.*). The reaction was repeated with 1-naphthyl isocyanate (338 mg, 2 mmol) as the electrophile. The product, tricarbonyl-η⁶-[1,3-di-1-naphthylquinazoline-2,4-dione]chromium(0) (337 mg, 61%) was isolated as a red crystalline solid, m.p. 200 °C (decomp.); $\nu_{max.}$ (Nujol) 1 965, 1 910, 1 865, 1 720, 1 680, 765, 660, and 610 cm^{-1}; δ($CDCl_3$) 4.5—5.2 (m), 5.4—5.6 (m), 6.5—6.7 (4 H, m), and 7.3—8.2 (14 H, m); *m/z* 550 (M^+), 466, and 414 (Found: C, 67.6; H, 3.25; N, 5.15. $C_{31}H_{18}CrN_2O_5$ requires C, 67.64; H, 3.29; N, 5.09%).

* In ref. 10, the authors did not isolate this complex but converted it immediately into the decomplexed material.

Phenyl isothiocyanate. The general procedure was repeated with phenyl isothiocyanate (540 mg, 4 mmol) as the electrophile. The product tricarbonyl-η⁶-(1,3-diphenylquinazoline-2,4-dithione)chromium(0) (310 mg, 65%) was obtained as red crystals, m.p. 120 °C; $\nu_{max.}$ (Nujol) 1 955, 1 920, 1 895, 1 600, 1 585, 700, 655, and 610 cm^{-1}; δ(CDCl$_3$) 4.6—4.8 (1 H, m), 4.9—5.6 (2 H, m), and 6.6—3.7 (11 H, m); *m/z* 482 (M^+), 398, and 346 (Found: C, 57.25; H, 2.9; N, 5.8. $C_{23}H_{14}CrN_2O_3S_2$ requires C, 57.25; H, 2.89; N, 5.81%).

Diphenylketene. The reaction was repeated using diphenylketene (200 mg, 1.04 mmol) as the electrophile. The product (10; R = COCHPh$_2$) (330 mg, 77%) was isolated as a red crystalline solid, m.p. 103—105 °C; $\nu_{max.}$ (Nujol) 1 975, 1 920, 1 890, 1 680, 670, 655, 620, and 610 cm^{-1}; δ(CDCl$_3$) 4.7—5.3 (2 H, m), 5.4—5.72 (m), 5.72 (2 H, s), 6.0—6.4 (1 H, m), and 7.30 (10 H, s); *m/z* 426 (M^+), 370, 342, and 290 (Found: C, 64.5; H, 3.5. $C_{23}H_{15}CrFO_4$ requires C, 64.79; H, 3.55%).

4,4-*Dimethyl*-3-*phenyloxazolidine*-2,5-*dione*. The general procedure was carried out using 4,4-dimethyl-3-phenyloxazolidine-2,5-dione * (205 mg, 1 mmol) as the electrophile. The product (10; R = COCMe$_2$NHPh) (239 mg, 61%) was isolated as a red crystalline solid, m.p. 127—128 °C; $\nu_{max.}$ (Nujol) 3 430, 3 400, 1 980, 1 925, 1 890, 1 680, 1 665, 695, 655, and 615 cm^{-1}; δ(CDCl$_3$) 1.59 (3 H, s), 1.68 (3 H, s), 4.12 (1 H, s, NH), 4.71 (1 H, m), 5.20 (1 H, m), 5.54 (1 H, m), 6.08 (1 H, m), 6.47 (2 H, m), 6.71 (1 H, m), and 7.12 (2 H, m); *m/z* 393 (M^+), 337, 309, and 289 (Found: C, 57.95; H, 4.05; N, 3.55. $C_{19}H_{16}CrFNO_4$ requires C, 58.01; H, 4.10; N, 3.56%).

(S)-3-*Isobutyl*-4-*isopropyloxazolidine*-2,5-*dione*. The general procedure was repeated using (*S*)-3-isobutyl-4-isopropyloxazolidine-2,5-dione * (199 mg, 1 mmol) as the electrophile. The product [10; R = COCH(Pr^i)NHBu^i] (143 mg, 37%) was then isolated as a red oil; $\nu_{max.}$ (neat) 3 350, 3 080, 2 950, 1 980, 1 910, 1 665, 1 600, 660, 640, and 615 cm^{-1}; δ(CDCl$_3$) 0.7—2.5 (10 H, m), 3.68 (1 H, br s), 4.7—5.1 (1 H, m), 5.1—5.5 (1 H, m), 5.5—5.9 (1 H, m), and 6.0—6.4 (1 H, m); *m/z* 387 (M^+), 331, 313, and 283 (Found: *m/z* 387.0930. $C_{18}H_{18}CrFNO_3$ requires *m/z* 387.0938).

4,4-*Dimethyl*-2-*phenyloxazolin*-5-*one*. The reaction was repeated using 4,4-dimethyl-2-phenyloxazolin-5-one [15] (190 mg, 1 mmol) as the electrophile. The product (10; R = COCMe$_2$NHCOPh) (300 mg, 75%) was isolated as a red crystalline solid, m.p. 167—168 °C; $\nu_{max.}$ (Nujol) 1 975, 1 905, 1 860, 1 820, 1 720, 1 660, 1 605, 700, 655, 635, and 610 cm^{-1}; δ(CDCl$_3$) 1.59 (3 H, s), 1.87 (3 H, s), 4.65—4.75 (1 H, m), 5.0—5.1 (1 H, m), 5.45—5.55 (1 H, m), 5.95—6.10 (1 H, m), and 7.4—7.7 (5 H, m); *m/z* 401 (M^+), 345, 317, and 265 (Found: C, 59.9; H, 3.75; N, 3.5. $C_{20}H_{15}CrNO_5$ requires C, 59.85; H, 3.77; N, 3.49%).

4-*Benzylidene*-2-*phenyloxazolin*-5-*one*. The general procedure was repeated using 4-benzylidene-2-phenoxazolin-5-one [16] (270 mg, 1.1 mmol) as the electrophile. The product [10; R = COC(NHCOPh)CHPh] (353 mg, 73%) was isolated as a red oil which could not be crystallised.

A sample of the product (300 mg, 0.62 mmol) was dissolved in THF and irradiated with a tungsten lamp in the presence of air for 2 days. The resulting mixture was filtered through silica H and the solvent evaporated to give 1-(α-benzamidocinnamoyl)-2-fluorobenzene (194 mg, 90%) as a white crystalline solid, m.p. 132—133 °C (from chloroform–petroleum); $\nu_{max.}$ (Nujol) 3 320, 1 650, 1 640, 1 625, 1 605, 760, 710, and 695 cm^{-1}; *m/z* 345 (M^+) and 105 (Found: C, 76.5; H, 4.75; N, 4.0. $C_{22}H_{16}FNO_2$ requires C, 76.51; H, 4.67; N, 4.05%).

N-*Methylbenzo*[d]*oxazine*-2,6-*dione*. The reaction was carried out using *N*-methyl-benzo[*d*]oxazine-2,6-dione [17] (177 mg, 1 mmol) as the electrophile. The product (195 mg, 53%) was isolated as a red crystalline solid, m.p. 168—170 °C; $\nu_{max.}$ (Nujol) 3 500—3 200, 1 965, 1 920, 1 900, 1 885, 1 615, 660, and 620 cm^{-1}; δ_H(CDCl$_3$) 2.90 (3 H, d, *J* 6 Hz), 4.6—5.0 (1 H, m), 5.0—5.9 (3 H, m), 6.5—7.7 (4 H, m), and 8.5—9.0 (1 H, br m); *m/z* 365 (M^+), 309, and 281 (Found: C, 55.75; H, 3.35; N, 3.85. $C_{17}H_{12}CrFNO_4$ requires C, 55.89; H, 3.31; N, 3.83%).

Cyclisation of Complex (10; R = COCMe$_2$NHPh). A solution of complex (10; R = COCMe$_2$NHPh) (460 mg, 1.17 mmol) in THF (20 ml) was added to a solution of lithium diisopropylamide (1.2 mmol, 1 equiv.) in THF (50 ml) at −78 °C. After 4 h, the reaction was warmed to room temperature and allowed to proceed overnight (16 h). Work-up with dilute hydrochloric acid, extraction into ether, drying of the ethereal layer (K_2CO_3), and evaporation of solvents gave a red oil which was purified by column chromatography (ether–petroleum). Tricarbonyl-η⁶-(5,5-dimethyl-1-phenylbenzo[*b*]-pyrrolin-4-one)chromium(0) (419 mg, 96%) was isolated as a red crystalline solid, m.p. 143 °C (decomp.); $\nu_{max.}$ (Nujol) 1 980, 1 900, 1 860, 1 700, 705, 670, and 615 cm^{-1}; δ(CDCl$_3$) 1.20 (3 H, s), 1.50 (3 H, s), 4.5—6.55 (4 H, m), and 7.2—7.6 (5 H, m); *m/z* 373 (M^+), 317, 289, and 237 (Found: C, 61.15; H, 4.1; N, 3.85. $C_{19}H_{15}CrNO_4$ requires C, 61.13; H, 4.05; N, 3.75%).

* Prepared according to the method of A. C. Farthing and R. J. W. Reynolds, *Nature*, 1950, **165**, 647.

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