ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 604 (2000) 157–169

Journal of Organometallic Chemistry

Novel synthesis of indazoles from (η^6-arene)tricarbonylchromium complexes

M. Rute G. da Costa [a,*], M. João M. Curto [a], Stephen G. Davies [b], M. Teresa Duarte [c], C. Resende [c], Fátima C. Teixeira [a,b]

[a] *Departamento de Tecnologia de Indústrias Químicas, Instituto Nacional de Engenharia e Tecnologia Industrial, Estrada do Paço do Lumiar 22, 1649-038 Lisbon, Portugal*

[b] *The Dyson Perrins Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QY, UK*

[c] *Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisbon, Portugal*

Received 29 February 2000; accepted 3 April 2000

Abstract

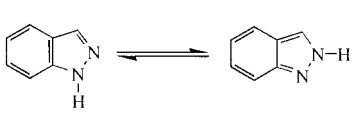
Indazole chromium complexes and some of its derivatives were synthesised by two strategies: (1) by cyclisation of [η^6-2-(2′-phenylhydrazine)-1,3-dioxolane]tricarbonylchromium (**2**) in acidic conditions which was converted into σ-complex (**11**); (2) by thermolysis of $Cr(CO)_6$ with 1-bis(trimethylsilyl)methylindazole (**3**) and 2-bis(trimethylsilyl)methyl-3-trimethyl-silylindazole (**4**), using bulky protecting groups at N(1) or simultaneously at N(2) and C(3), to afford [η^6-1-bis(trimethylsilyl)methylindazole]tricarbonylchromium (**14**) and [η^6-2-bis(trimethylsilyl)methyl-3-trimethylsilylindazole]tricarbonylchromium (**15**), respectively. The deprotonation of complex **14** followed by electrophilic quench occurs at the C(4) and C(7) positions in a ratio of 3:1 and with complex **15** the deprotonation was completely regioselective at the C(7) position. The position of this substitution was confirmed by n.O.e. difference spectroscopy and X-ray crystal structure determination of the [η^6-2-bis(trimethylsilyl)methyl-7-methyl-3-trimethylsilylindazole]tricarbonylchromium (**5**). These complexes were decomplexed to produce new substituted indazole derivatives in good yield.

Keywords: Indazoles; Arene complexes; Hetero arene complexes; Chromium

1. Introduction

The annular tautomerism of indazole (**1**) concerns the position of the NH proton, the benzenoid 1*H*-tautomer (**1a**) being always more stable than the quinonoid 2*H*-tautomer (**1b**) (Scheme 1) [1–3].

The two known examples of natural products containing an indazole ring nucleus — nigellicine and nigellidine — were isolated from *Nigella sative* Linn. (Rannunculaceae) and are used for the treatment of various diseases [4]. Although the indazole ring system is not abundant in nature, a number of its derivatives have been synthesised and several display a wide variety of applications in the fields of agriculture, industry and biology, while some are effective pharmacophores in medicinal chemistry [1,2,5,6]. From literature results, it appears that changes in the basicity–acidity of 1*H*- and 2*H*-indazole derivatives dramatically changes their biological activity [6i].



1a **1b**

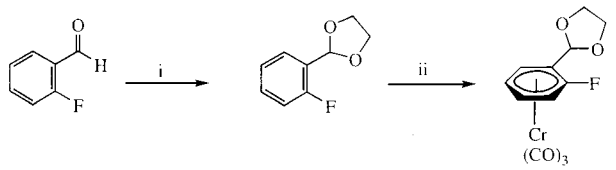
Scheme 1. Annular tautomerism of indazole (Benzenoid 1*H*-indazole tautomer (**1a**); quinonoid 2*H*-indazole tautomer (**1b**)).

There are three classical ways to prepare indazoles and several improved syntheses have been developed. These syntheses proceed from benzene derivatives, where the pyrazole ring was generated by ring closure [1,7].

The indazole ligand has been used as a nitrogen σ donor in organometallic chemistry [2,8–14] and until now there are no reports of indazole–chromium complexes. The tricarbonylchromium complexes of hetero-

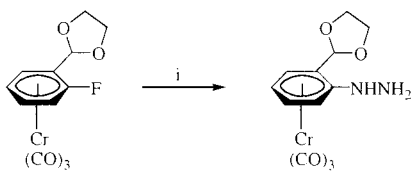
* Corresponding author.

0022-328X/00/$ - see front matter
PII: S0022-328X(00)00215-1



7 8 9

Scheme 2. Reagents and conditions: (i) $HOCH_2CH_2OH$, *p*-$TsOH{\cdot}H_2O$, C_6H_6; (ii) $Cr(CO)_6$, Bu_2O:THF (10:1).



9 2

Scheme 3. Reagents and conditions: (i) $NH_2NH_2.H_2O$, THF, Δ.

cycles were prepared for the first time by Fischer [15]. There are a large of known tricarbonylchromium complexes from heterocycles, but usually involve only one heteroatom [16–22]. These heterocyclic π-complexes are difficult to prepare because the nitrogen lone pair of electrons compete with the carbocyclic ring in coordination to the metal, forming σ-coordinated complexes. In the complexation of condensed heterocycles with two heteroatoms, such as benzoxazole and benzimidazole, Toma observed that the main product was the $N–Cr(CO)_5$ complex [18].

To the best of our knowledge we report herein the first examples of indazole–chromium complexes synthesised by formation of a pyrazole ring via cyclisation of [η^6-2-(2′-phenylhydrazine)-1,3-dioxolane]tricarbonylchromium (**2**) or by π-coordination of the tricarbonylchromium moiety to the arene ring of 1-bis-(trimethylsilyl)methylindazole (**3**) and 2-bis(trimethylsilyl)methyl-3-trimethylsilylindazole (**4**), using bulky TMS groups.

After the preparation of the π-complexes we examined their deprotonation–electrophilic sequences to afford new indazole derivatives, following decomplexations. In addition, we disclosed the details of the crystal structure of complex **5** which showed its exclusive regioselectivity at C(7).

2. Results and discussion

Our initial efforts to form an indazole–chromium complex focused on the cyclisation of a di-substituted aromatic complex. Different cyclisation approaches to the synthesis of indazole proceed from benzene derivatives, where the pyrazole moiety was generated by ring closure [1,7]. So logical disconnection of the indazole tricarbonylchromium complex was examined, assuming that the starting material must coordinate to tricarbonylchromium moiety very easily and the resulting complex must be a stable di-substituted aromatic complex.

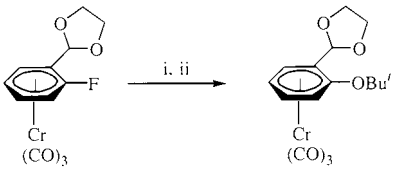
The retrosynthetic analysis from (η^6-indazole)tricarbonylchromium (**6**) shown that the best route for disconnection starts from 2-fluorobenzaldehyde (**7**). As (η^6-2-fluorobenzaldehyde)tricarbonylchromium complex can not be prepared by direct complexation with $Cr(CO)_6$, we synthesised 2-(2′-fluorophenyl)-1,3-dioxolane (**8**) according to the literature [23]. Thermolysis of $Cr(CO)_6$ with 2-(2′-fluorophenyl)-1,3-dioxolane (**8**) gave, after work-up, complex **9** as a yellow solid in 44% yield (Scheme 2). Spectroscopic data for this complex are in agreement with those reported in the literature [23]. Tricarbonylchromium complexes of phenyl halides undergo nucleophilic substitution (*ipso* substitution) of halogen by nucleophiles, therefore the reaction of complex **9** and hydrazine gave, after work-up, chromatography and recrystallisation, complex **2** as yellow crystals in 15% yield (Scheme 3).

To improve the yield of this nucleophilic substitution, distinct conditions were used which are described in Table 1. The best conditions for the substitution reaction in order to obtain compound **2** were achieved when this reaction was carried out with 2.5 equivalents of hydrazine and refluxed over 2 days (Table 1). Using complex **9** with hydrazine in the presence of potassium *tert*-butoxide, complex **10** was isolated in 96% yield (Scheme 4) and was totally characterised.

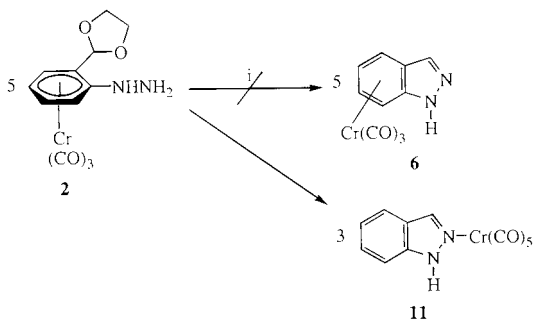
Subsequent research was directed towards formation of the pyrazole ring of indazole by a cyclisation reaction. Using a solution of complex **2** in CH_2Cl_2 and a catalytic quantity of (±)-camphorsulfonic acid, after 5 min, the colour of the mixture changed from yellow to red. The ^{1}H-NMR spectrum of the crude reaction

Table 1
Experimental conditions for the synthesis of complex **2**

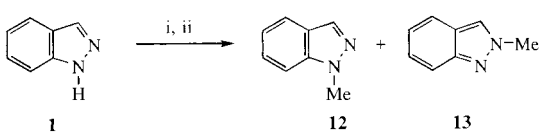
Hydrazine (equivalents)	Base	Reaction time (h)	Yield of **2** (%)
1.5		18	15
2.0		48	29
2.5		48	54
5		72	31
1.5	$NaHCO_3$ (2 equivalents)	96	26



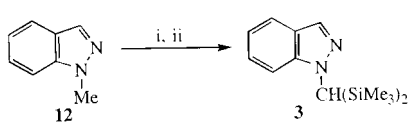
Scheme 4. Reagents and conditions: (i) $NH_2NH_2.H_2O$, THF; (ii) *t*-BuOK, 18 h, Δ.



Scheme 5. Reagents and conditions: (i) CSA, CH_2Cl_2, r.t.



Scheme 6. Reagents and conditions: (i) *n*-BuLi or NaH; (ii) MeI.



Scheme 7. Reagents and conditions: (i) *t*-BuLi; (ii) TMSCl.

mixture showed only the presence of the σ-complex **11**. The mixture was purified by column chromatography to give yellow crystals of compound **11** in 62% yield (Scheme 5). The ^{1}H-NMR spectrum of this yellow σ-complex was identical to the ^{1}H-NMR spectrum of the same complex when the free indazole is submitted to direct complexation with $Cr(CO)_6$ in which the chromium moiety is σ-bonded to the nitrogen lone pair of electrons. This lone pair is in the same plane as the pyrazole ring and it has a greater tendency to coordinate to the chromium moiety. The carbon signals on the ^{13}C-NMR spectrum were only very slightly shifted relative to the free indazole, except a slight deshielding of the C(3) signal (δ 142.16) compared with the free ligand (δ 135.2) [13]. Infrared analysis showed the presence of the extremely strong carbonyl stretching frequencies at 1970 and 1903 cm^{-1} and the presence of the pentacarbonylchromium fragment was also confirmed by mass spectrometry ($m/z = 310$, M^+). All spectroscopic data for this complex showed clearly that no π-complex was present and confirmed the presence of a σ-complex **11**. This cyclisation reaction was repeated using *p*-toluenesulfonic acid, after work-up complex **11** was isolated in 64% yield.

To confirm the nature of complex **11** obtained by the procedures described above, an ether solution of this complex was exposed to air and light. The colourless solution was filtered through Celite® and the solvent removed to afford a colourless oil and its ^{1}H-NMR spectrum proved it to be identical with the 1*H*-indazole reported in the literature [13].

The formation of the indazole by cyclisation of complex **2** was observed, but the transference of the chromium fragment to the nitrogen atom makes this route unsuccessful for the synthesis of the π-complex **6**. Hence, any approach to the synthesis of an indazole π-complex could be via the preparation of a protected indazole to prevent σ-complexation.

Strategies for the formation of π-complexes of pyridines [20,21], thiophenes [22], benzothiazoles and benzimidazoles [24] have demonstrated the usefulness of alkylsilyl groups or other bulky groups. Thus, a similar strategy was envisaged to increase steric hindrance at the nitrogen atoms of indazole.

N-Methylation of indazole (**1**) with *n*-BuLi–MeI at −78°C afforded a mixture of 1-methylindazole (**12**) and 2-methylindazole (**13**) which were separated by chromatography, giving white crystals in 58 and 40% yield, respectively (Scheme 6), whose the unambiguous assignment was carried out by ^{1}H- and ^{13}C-NMR spectra [3,25–30].

This reaction was also carried out using NaH as a deprotonating agent, in which case compounds **12** and **13** were isolated in 52 and 40% yield, respectively.

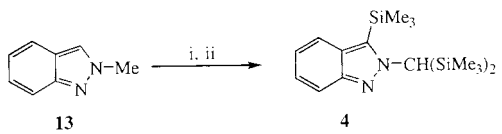
To protect both nitrogen lone pair of electrons, a subsequent deprotonation of 1-methylindazole (**12**) and 2-methylindazole (**13**) with base, followed by electrophilic quench with TMSCl was developed.

Thus, 1-methylindazole (**12**) reacted with *t*-BuLi (3.5 equivalents)–TMSCl at −78°C to form 1-bis(trimethylsilyl)methylindazole (**3**) in 73% yield (Scheme 7) which is in agreement with Tertov's results [31], who has used *n*-BuLi at −15°C. The ^{1}H-NMR spectrum of **3** shows a singlet at δ 0.06 attributed to two TMS groups and one proton singlet at δ 3.55 attributed to a methine proton which confirms this deprotonation. The presence of a proton singlet at δ 7.94 confirms that the H(3) position was not silylated.

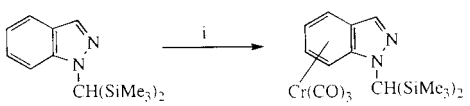
2-Methylindazole (**13**) also reacted with *t*-BuLi–TMSCl in the above experimental conditions to form 2-bis(trimethylsilyl)methyl-3-trimethylsilylindazole (**4**) as a colourless oil in 98% yield. The metallation occurred simultaneously at two adjacent non-equivalent groups (Scheme 8). These observations were confirmed by ^{1}H- and ^{13}C-NMR spectroscopies which showed the presence of the TMS signals, with the C(3) signal appearing

as a C_{ipso} (δ 132.84). Similar results were documented by Tertov [31] who found that 1-methylindazole (**12**) was metallated by *n*-BuLi (-15°C) at the *N*-methyl group and 2-methylindazole (**13**) was only lithiated at the 3-position. Using *t*-BuLi we also observed metallation of the *N*-methyl group of the 2-methylindazole (**13**).

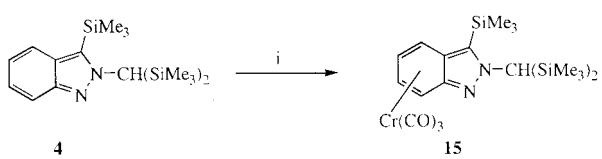
Directed complexation of compound **3** and **4** with $Cr(CO)_6$ under reflux afforded complexes **14** and **15** in 60 and 92% yield, respectively, Bu_2O–*n*-heptane being the most effective solvent systems (Schemes 9 and 10).



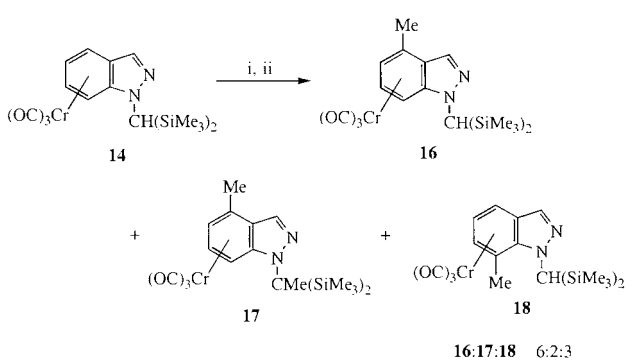
Scheme 8. Reagents and conditions: (i) *t*-BuLi; (ii) TMSCl.



Scheme 9. Reagents and conditions: (i) $Cr(CO)_6$, Bu_2O–*n*-heptane (1:1), Δ, 6 days.



Scheme 10. Reagents and conditions: (i) $Cr(CO)_6$, Bu_2O–*n*-heptane (1:1), Δ, 6 days.



Scheme 11. Reagents and conditions: (i) *n*-BuLi–TMEDA; (ii) MeI.

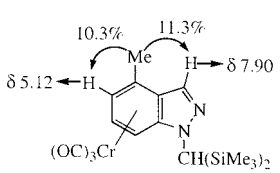


Fig. 1. n.O.e. difference spectroscopy of complex **16**.

^{1}H-NMR spectra analysis of these complexes showed four up-field resonances relative to the carbocyclic protons, strong evidence for the presence of a π-complex with the carbocyclic ring. ^{13}C-NMR spectra also confirmed these attributions.

As expected from the literature [16], the complexation occurred on the carbocyclic ring rather than to the pyrazole ring. These reactions also showed that the use of sterically demanding TMS groups provide ample steric hindrance at the nitrogen lone pair and promote π-complexation on the carbocyclic ring, eliminating the possibility of σ-coordination with nitrogen. The π-bonding of the tricarbonylchromium fragment to the carbocyclic ring of the protected indazoles described here, is consistent with the behaviour of other condensed heterocycles, such as indole [16], quinaldine [17], benzothiophene [16,19] and benzofuran [16].

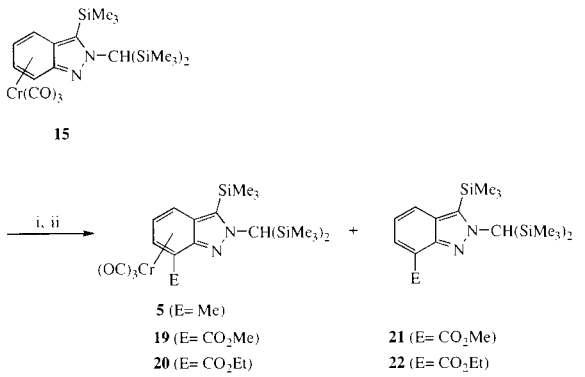
The tricarbonylchromium unit in these π-complexes creates the potential for promoting substitution in the carbocyclic ring. This enables proton abstraction to occur in conditions under which the uncomplexed substrate is unreactive. Subsequent efforts were directed towards the investigation of the effect of deprotonation agents upon complexes **14** and **15**.

Treatment of complex **14** with *n*-BuLi–TMEDA in THF, followed by MeI quenching gave a red oil. ^{1}H-NMR spectrum of the crude reaction mixture showed the presence of complexes **16**, **17** and **18** in a ratio 6:2:3 (Scheme 11). Column chromatography allowed isolation of 4- and methine-substituted indazole complex **17** in 11% yield. However, despite careful and repeated attempts to separated complexes **16** and **18**, only the major 4-substituted indazole **16** was isolated in 24% yield, after repeated recrystallisations.

The structure of complex **16** was assigned to a 4-substituted indazole complex by nuclear Overhauser effect (n.O.e) difference spectroscopy. Irradiation of the CH_3 protons at the 4-position results in the enhancement in the H(5) and H(3) resonances (Fig. 1). All the data for this complex were consistent with the proposed structure.

The structure assignment of complex **17** was based on its ^{1}H-NMR spectrum which showed the presence of three contiguous protons in the complexed arene ring, one proton singlet at δ 7.86 attributed to H(3) of the pyrazole nucleus and two singlets each one relative to three protons at δ 2.04 and the other at δ 2.63 due to two new methyl groups. The ^{13}C-NMR spectrum, with the characteristic carbon signal at high field attributed to C(7), is similar to that of complex **16** and similar to literature data [3].

Complex **18** could not be isolated pure, but the ^{1}H-NMR spectrum of its mixture with complex **16** allowed to assign complex **18** as the 7-substituted isomer.



Scheme 12. Reagents and conditions: (i) *n*-BuLi–TMEDA; (ii) E^+.

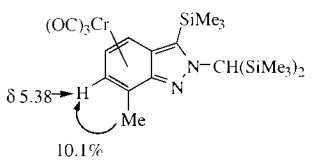


Fig. 2. n.O.e. difference spectroscopy of complex **5**.

This deprotonation–methylation sequence was repeated in the absence of TMEDA by a similar procedure. Analysis of the crude product by ^{1}H-NMR spectroscopy demonstrated that only complexes **16** and **18** were formed in a ratio 3:1. Under these experimental conditions, the deprotonation–methylation sequence of complex **14** resulted in 4- and 7-substituted indazoles, **16** and **18**, respectively, the 4-substituted complex being the major complex. Presumably, the steric effect of the bulky bis(trimethylsilyl)methyl group present in complex **14** generates steric hindrance and disfavours deprotonation at the 7-position, with deprotonation of 4-position predominating. In contrast to the uncomplexed indazole [32], this strategy allowed the formation of the 4-substituted indazole derivatives and no 5-substituted derivative was produced [1,2].

The first strategy for the deprotonation–electrophilic quench sequence outlined for complex **14** was extended to complex **15**. Lithiation of complex **15** with *n*-BuLi–TMEDA or *n*-BuLi, followed by MeI quench, afforded only the 7-substituted indazole complex **5** (Scheme 12). With *n*-BuLi–TMEDA the yield of the complex **5** was much better (81%) than in *n*-BuLi (20%).

The ^{1}H-NMR spectrum of complex **5** indicated the presence of three contiguous protons in the complexed homocyclic ring and a three protons singlet at δ 2.67 due to the new methyl substituent in complex **5**. The structure of complex **5** was initially assigned by n.O.e. difference spectroscopy. Irradiation of the methyl protons of the electrophile at δ 2.72 results in the enhancement of the H(6) resonance and no enhancement in the resonance of the TMS protons at C(3) (Fig. 2). These observations were only consistent with a 7-substituted indazole complex derivative.

At the single crystal X-ray structure analysis of complex **5**, two geometrically identical molecules were found in the asymmetric unit. Fig. 3a shows the molecular diagram while Table 2 displays selected bond lengths and angles. The coordination geometry around the chromium is the usual for these (η^6-arene)tricarbonylchromium complexes, the so called three legged piano stool. The indazole ring is planar with maximum deviations of $\pm$0.049(7) Å to the mean least squares plane. Atoms C(8), C(9), H(9) and Si(1) are also in the plane of the ring. The chromium is at an average distance of 1.758(4) Å from the carbocyclic ring, even though atoms C(3a) and C(7a) present a slight longer bonding distance, 2.319(5) and 2.329(6) Å,

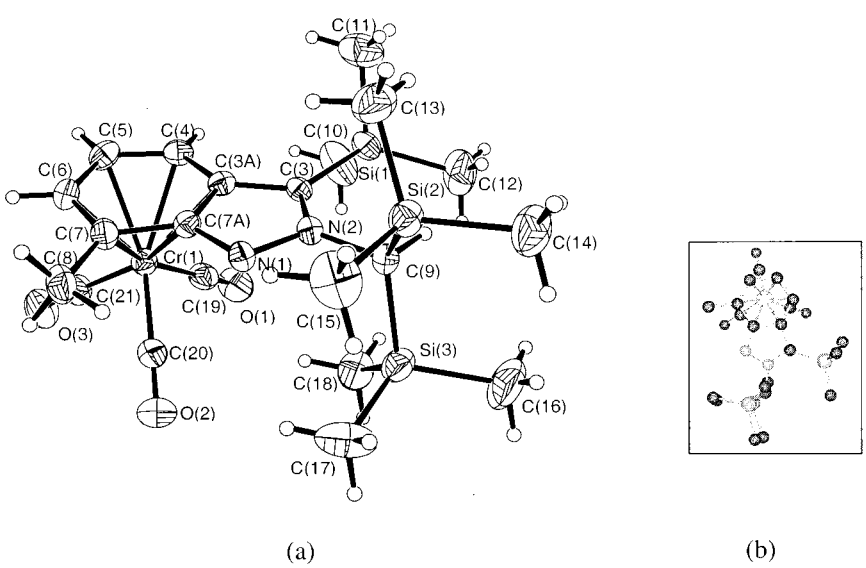
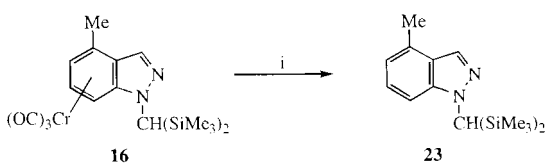


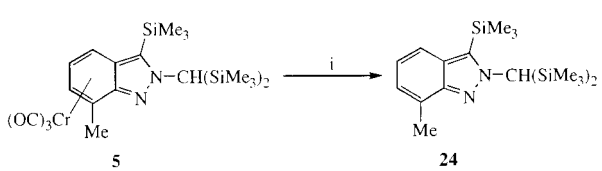
Fig. 3. (a) Molecular diagram of complex **5** and (b) view of the molecule showing the relative positions of carbonyl ligands to the carbocyclic ring.

Table 2
Selected bond lengths (Å) and angles (°) for complex **5**

Bond length	
Cr(1)–C(20)	1.827(7)
Cr(1)–C(21)	1.832(7)
Cr(1)–C(19)	1.846(7)
Cr(1)–C(5)	2.198(6)
Cr(1)–C(6)	2.201(6)
Cr(1)–C(4)	2.224(6)
Cr(1)–C(7)	2.261(6)
Cr(1)–C(3a)	2.319(5)
Cr(1)–C(7a)	2.329(6)
C(3)–N(2)	1.354(7)
C(3)–C(3a)	1.421(7)
C(3a)–C(7a)	1.428(7)
C(7a)–N(1)	1.344(7)
C(7a)–C(7)	1.425(7)
C(7)–C(6)	1.386(8)
C(7)–C(8)	1.489(9)
C(6)–C(5)	1.404(9)
C(5)–C(4)	1.397(8)
N(1)–N(2)	1.365(6)
N(2)–C(9)	1.462(7)
Bond angles	
C(20)–Cr(1)–C(21)	86.7(3)
C(20)–Cr(1)–C(19)	90.0(3)
C(21)–Cr(1)–C(19)	86.9(3)
C(3)–N(2)–C(9)	129.2(4)
N(1)–N(2)–C(9)	115.1(4)
N(2)–C(9)–Si(3)	111.0(4)
N(2)–C(9)–Si(2)	109.5(4)
Si(3)–C(9)–Si(2)	120.4(3)



Scheme 13. Reagents and conditions: (i) hν, O_2.



Scheme 14. Reagents and conditions: (i) hν, O_2.

respectively (see Table 2). All the distances within the carbocyclic ring are as found in other related compounds [13,19,33].

The results of X-ray structural analysis of complex **5** clearly confirmed that substitution occurred at the C(7) position and the carbocyclic ring was η^6-coordinated to the tricarbonylchromium fragment. It could also be seen that the most stable conformation of complex **5** is the one where the two TMS substituents at N(2) are in opposite direction with respect to the TMS group at the C(3) position, with the methine proton in the same direction of the 3-substituent (Fig. 3a).

A view of the structure from the uncomplexed face of the indazole complex **5** shows the tricarbonylchromium tripod with respect to the carbocyclic ring, rotated away from the ideally staggered conformation, with the carbonyl groups located between C(5) and C(6) and near C(4) and C(7) (Fig. 3b). This is indicative of enhanced electron deficiency at C(4) and C(7) and thus enhanced the anion stabilisation at these centers [34].

The origins of the regioselective deprotonation can be rationalised in terms of chelation control and steric effect. Coordination of the lithium cation to the nitrogen lone pair of electrons at N(1) could increase the acidity of the 7-position, giving rise to selective removal of the proximal C(7) hydrogen to produce the corresponding stabilised anion. The deprotonation of the C(4) position is precluded in this case, because the very bulky TMS group at C(3) position prevent approach of the bases employed to the C(4) hydrogen. The selected deprotonation–electrophilic sequence of complex **15** leads to a total regioselectivity at C(7), in contrast to the deprotonation of complex **14** and the electrophilic substitution of the uncomplexed 2*H*-indazole [1,32].

With the structure of complex **5** established, the lithiated complex was treated with other electrophiles ($ClCO_2Me$ and $ClCO_2Et$) to give substituted indazole complexes **19** and **20** (Scheme 12). In both cases the 7-substituted complex **19** and **20** were isolated in pure form by column chromatography in 25 and 26% yield, respectively. The corresponding decomplexed indazoles **21** and **22** were also isolated in 33 and 40% yield, respectively. These compounds were fully characterised and data are in agreement with the proposed structures.

Complexes **16** and **5** were subject to decomplexation reactions, by exposing ether solutions of both complexes to air and light until the yellow colour of the solutions disappeared. Filtration to remove chromium(III) residues, followed by evaporation of the filtrate afforded the decomplexed indazoles **23** and **24**, respectively (Schemes 13 and 14). ^{13}C-NMR spectroscopy showed the absence of the carbonyl signals and infrared analyses confirmed the removal of the tricarbonylchromium moiety in both cases.

Desilylation at the C(3), N(2) or N(1) positions of these compounds can easily be carried out by known procedure to afford the corresponding free indazole derivatives [35].

3. Conclusions

We reported the synthesis of the first indazole chromium complexes. The cyclisation of [η^6-2-(2′-phenylhydrazine) - 1,3 - dioxolane]tricarbonylchromium (**2**) afforded the indazole σ-complex (**11**) only.

The π-complexes [η^6-1-bis(trimethylsilyl)methylindazole]tricarbonylchromium (**14**) and [η^6-2-bis(trimethylsilyl)methyl - 3 - trimethylsilylindazole]tricarbonylchromium (**15**) were successfully prepared for the first time via direct complexation of hindered silylated compounds **3** and **4**, respectively.

Establishment of experimental conditions of deprotonation–electrophilic sequence of complexes **14** and **15** allowed to determine their regioselectivity. In complex **14** the nature of carbanion and the steric hindrance of substituents on the indazole created more than one position for electrophilic attack on the indazole complex, the 4-substituted complex **16** being the major complex formed. In complex **15** we have established the exclusive C(7) funcionalisation which will allow the development of the synthesis of a great variety of C(7) functionalised indazoles.

4. Experimental

All the reactions involving air sensitive reagents and organometallic complexes, as well as their purification, were performed under an atmosphere of dry nitrogen and all solvents were degassed before use. All solvents were distilled under a nitrogen atmosphere. Diethyl ether (referred to ether), THF, dibutyl ether (Bu_2O) and dioxane were distilled from Na–benzophenone ketyl. CH_2Cl_2 was distilled from calcium hydride. 'Petroleum ether' (petrol) refers to the fraction distilling between 40 and 60°C and was redistilled before use. Reagents were used as purchased and when necessary were purified according to standard procedures [36]. *n*-BuLi was used as a 1.3–1.6 M solution in hexane and *t*-BuLi as a 1.0–1.7 M solution in hexane and were titrated immediately before use. NaH was used as 60% dispersion in mineral oil, which was washed with petrol and dried in vacuo before use. Column chromatography was performed on silica gel (230–400 Mesh) under a positive pressure of nitrogen. Melting points were determined on a Reichert Thermovar or on a Gallenkamp melting point apparatus and are uncorrected. Infrared spectra were recorded using a Perkin–Elmer 172SX Fourier Transform or a Perkin–Elmer 781 instrument. ^{1}H-NMR spectra were recorded at 200 MHz on a Varian Gemini 200 or a Bruker AC 200 spectrometer, or at 300 MHz on a General Electrical QE-300 spectrometer. ^{13}C-NMR spectra were recorded at 75 MHz on a General Electrical QE-300 spectrometer or a Bruker WH 300 spectrometer, or at 125 MHz on a Bruker AMX 500 spectrometer. NMR spectra were recorded in $CDCl_3$, using tetramethylsilane (δ_H 0.00 ppm) or residual $CHCl_3$ (δ_H 7.26 ppm; δ_C 77.0 ppm) as internal standard. Chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. Mass spectra (m/z) were recorded on a Kratos 25 RF, a VG MicromassLab ZAB 1F, a VG MassLab 20–250 or an APCI Plataform spectrometer. High resolution mass spectra (HRMS) were obtained on a VG AutoSpect instrument. Elemental analysis were performed on a Carlo Erba 1106 elemental analyser.

[2-(2′-Fluorophenyl)-1,3-dioxolane] (**8**) and [η^6-2-(2′-fluorophenyl)-1,3-dioxolane]-tricarbonylchromium (**9**) were prepared according to the literature [23] and the spectroscopic data were identical with those reported.

4.1. [η^6-2-(2′-Phenylhydrazine)-1,3-dioxolane]-tricarbonylchromium (2)

To a solution of complex **9** (201 mg, 0.66 mmol) in THF (40 ml) was added hydrazine hydrate (0.08 ml, 1.65 mmol) and the mixture was heated at reflux for 2 days. The solution was filtered through silica, eluted with ethyl acetate and the solvents were removed in vacuo to give a yellow oil. Column chromatography (petrol–ether (7:3)), followed by recrystallisation from ether–petrol, gave complex **2** (113 mg, 54%) as yellow crystals. M.p. 120–121°C. IR ν_{max} (KBr): 3412, 3323 (N–H), 3096 (C–H)Ar, 2975, 2908 (C–H), 1964, 1867, 1830 (C≡O), 1638, 1546, 1485 cm^{-1} (C=C). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.53 (2H, br s, NH_2), 4.05 (2H, m, OCH_2CH_2O), 4.26 (2H, m, OCH$_2$CH_2O), 4.81 (1H, t, *J* 6.3, 4-H or 5-H), 5.55 (1H, d, *J* 6.9, 3-H or 6-H), 5.68 (1H, t, *J* 6.3, 5-H or 4-H), 5.72 (1H, s, OC*H*O), 5.84 (1H, d, *J* 6.3, 6-H or 3-H), 6.29 (1H, br s, N*H*). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 65.00 (O*C*H$_2$CH$_2$O), 65.46 (OCH$_2$*C*H$_2$O), 73.69, 82.19, 95.80, 96.90, 100.74 (Ar:C3–C6, O–*C*H–O), 89.92 (Ar:C1, C_{ipso}), 132.91 (Ar:C2, C_{ipso}), 234.11 (*C*O). m/z (EI): 316 (M$^+$, 11%), 260 (M$^+$ − 2CO, 3%), 232 (M$^+$ − 3CO, 3%), 180 [M$^+$ − Cr(CO)$_3$, 1%], 52 (Cr$^+$, 100%). Anal. Found: C, 45.81; H, 3.69; N, 8.86. Calc.: C, 45.58; H, 3.82; N, 8.86%.

4.2. [η^6-2-(2′-tert-Butoxyphenyl)-1,3-dioxolane]-tricarbonylchromium (10)

To a solution of potassium *tert*-butoxide (518 mg, 4.86 mmol) in THF (20 ml) at 0°C, was added hydrazine hydrate (0.15 ml, 3.09 mmol), followed by addition of complex **9** (468 mg, 1.54 mmol) in THF (30 ml). This mixture was heated at reflux for 18 h. The resulting solution was filtered through silica, eluted with ethyl acetate and the solvents were removed in vacuo to give complex **10** (529 mg, 96%) as yellow crystals. M.p. 91–92°C. IR ν_{max} (KBr): 3085 (C–H)Ar, 2977, 2931, 2895 (C–H), 1972, 1884, 1864 (C≡O), 1523, 1504, 1477 cm^{-1} (C=C). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.47 [9H, s, OC(CH_3)$_3$], 3.98–4.20 (4H, m, OCH_2CH_2O), 4.85 (1H, t, *J* 6.3, Ar*H*, 4-H or 5-H), 5.24 (1H, d, *J* 6.6, Ar*H*, 3-H or 6-H), 5.49 (1H, dt, *J* 6.3 and 1.2, Ar*H*,

5-H or 4-H), 5.84 (1H, dd, *J* 6.3 and 1.2, Ar*H*, 6-H or 3-H), 5.86 (1H, s, OC*H*O). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 28.75 [OC(CH_3)$_3$], 65.64 (OCH_2CH_2O), 82.09, 84.68, 92.82, 94.23, 98.38 (Ar:C3–C6, O–*C*H–O), 82.22 [O*C*(CH_3)$_3$, C_{ipso}], 97.09 (Ar:C1, C_{ipso}) 140.03 (Ar:C2, C_{ipso}), 232.80 (*C*O). *m*/*z* (EI): 358 (M^+, 22%), 302 ($M^+ - 2CO$, 6%), 274 ($M^+ - 3CO$, 17%), 173 ($C_7H_5O_2Cr^+$, 100%). Anal. Found: C, 53.38; H, 4.87. Calc.: C, 53.64; H, 5.06%

4.3. Preparation of (η^1-indazole)pentacarbonylchromium (**11**) via cyclisation of complex **2**

To a solution of complex **2** (40 mg, 0.13 mmol) in CH_2Cl_2 (10 ml) was added ($\pm$)-camphorsulfonic acid (5 mg). After stirring for 5 min at r.t., the solvent was evaporated. The residue was redissolved in ether, filtered through a plug of silica and the solvent was removed in vacuo. Purification of the resulting yellow oil by column chromatography (petrol–ether (1:1)) gave compound **11** (15 mg, 62%) as yellow crystals. M.p. (dec.) 113°C. IR ν_{max} (KBr): 3470 (N–H), 3078 (C–H)Ar, 1970 and 1903 (C≡O), 1629, 1510, 1439 cm^{-1} (C=C, C=N). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.20–7.24 (1H, m, Ar*H*), 7.46 (1H, m, Ar*H*), 7.48 (1H, m, Ar*H*), 7.68 (1H, d, *J* 8.2, Ar*H*), 8.08 (1H, d, *J* 1.5, 3-H), 9.89 (1H, br s, N*H*). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 108.94 (Ar:C7), 119.87, 122.50, 128.58 (Ar:C4–C6), 123.44 (Ar:C3a), 141.31 (Ar:C7a), 142.16 (Ar:C3), 214.20, 220.02 (*C*O). *m*/*z* (EI): 310 (M^+, 1%), 198 ($M^+ - 4CO$, 2%), 170 ($M^+ - 5CO$, 11%), 118 [$M^+ - Cr(CO)_5$, 100%]. Anal. Found: C, 46.21; H, 1.92; N, 8.84. Calc.: C, 46.47; H, 1.95; N, 9.03%.

4.4. Preparation of (η^1-indazole)pentacarbonylchromium (**11**) from indazole (**1**)

A solution of indazole (**1**) (500 mg, 4.23 mmol) and $Cr(CO)_6$ (1.12 g, 5.08 mmol), in Bu_2O (50 ml) and THF (5 ml), was heated at reflux for 4 days. The resulting yellow solution was filtered through silica, washed initially with petrol (100 ml) and then CH_2Cl_2 (200 ml) to yield a yellow solution. Evaporation of solvents in vacuo and recrystallisation from ether–*n*-hexane gave compound **11** (679 mg, 52%) as a yellow solid. M.p. (dec.) 113°C. All spectroscopic data were identical to the previously described.

4.5. Decomplexation of (η^1-indazole)pentacarbonylchromium (**11**)

A solution of complex **11** (30 mg, 0.097 mmol) in ether (15 ml) was exposed to air and sunlight. After 5 days, filtration through Celite® and evaporation of the solvent gave indazole (**1**) (10 mg, 88%) identical with an authentic sample.

4.6. Preparation of 1-methylindazole (**12**) and 2-methylindazole (**13**) using two different processes

4.6.1. Using *n*-BuLi as base

n-BuLi (9.0 ml, 11.70 mmol) was added dropwise to a solution of indazole (**1**) (1.07 g, 9.02 mmol) in THF (50 ml) at −78°C. After 30 min, the reaction mixture was warmed to 0°C, stirred over 15 min and then recooled to −78°C. After 15 min, excess MeI (1.7 ml, 27.3 mmol) was added and the reaction mixture was allowed to warm slowly to r.t. and stirred overnight. After quenching with methanol (1 ml), the solvent was removed under reduced pressure. The residue was redissolved in ether, filtered through a plug of magnesium sulfate and silica and the solvent removed in vacuo. Purification of the resulting pale yellow oil by column chromatography (petrol–ether (3:2)) gave the known 1-methylindazole (**12**) (690 mg, 58%), followed by 2-methylindazole (**13**) (481 mg, 40%), both as white crystalline solids. Compound **12**: M.p. 58°C ([27] 60–61°C). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.99 (3H, d, *J* 1.2, NCH_3), 7.07–7.13 (1H, m, Ar*H*), 7.31–7.34 (2H, m, Ar*H*), 7.68 (1H, d, *J* 8.1, Ar*H*), 7.95 (1H, s, 3-H). ^{13}C-NMR [29] (75 MHz, $CDCl_3$): δ 35.20 (NCH_3), 108.66 (Ar:C7), 120.18 (Ar:C5), 120.80 (Ar:C4), 123.77 (Ar:C3a), 125.94 (Ar:C6), 132.44 (Ar:C3), 139.62 (Ar:C7a). *m*/*z* (EI): 132 (M^+, 100%). Compound **13**: M.p. 56°C ([27] 56°C). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 4.19 (3H, s, NCH_3), 7.07 (1H, t, *J* 7.5, Ar*H*), 7.27 (1H, t, *J* 7.5, Ar*H*), 7.63 (1H, d, *J* 7.8, Ar*H*), 7.70 (1H, d, *J* 8.4, Ar*H*), 7.85 (1H, s, 3-H). *m*/*z* (EI): 132 (M^+, 100%).

4.6.2. Using NaH as base

A solution of indazole (**1**) (1.93 g, 8.72 mmol) in THF (10 ml) was added to a suspension of NaH (1.27 g, 42.3 mmol) in THF (25 ml). When no further gas was evolved, the mixture was cooled to 0°C and MeI (2.7 ml, 43.1 mmol) was added. The reaction mixture was stirred at r.t. overnight. Ether (150 ml) was added to the reaction mixture and the resulting solution filtered through Celite®. After evaporation of the solvents the resulting mixture was purified by column chromatography (petrol–ether (3:2)) to give 1-methylindazole **12** (630 mg, 52%) and 2-methylindazole **13** (460 mg, 40%), both as white crystalline solids.

4.7. 1-[bis(Trimethylsilyl)methyl]indazole (**3**)

t-BuLi (10.9 ml, 18.09 mmol) was added dropwise to a solution of compound **12** (680 mg, 5.15 mmol) in THF (20 ml). After stirring at −78°C for 2 h, TMSCl (2.6 ml, 20.49 mmol) was added and the reaction was stirred at −78°C for 1.5 h. Work-up was performed using the same procedure as in Section 4.6.1. Purification of the resulting orange oil by column chromatography (petrol–ether (9:1)) gave compound **3** (1.03 g,

73%) as white crystals. M.p. 58°C. IR ν_{max} (KBr): 3057, 3041 (C–H)Ar, 2955, 2898, 2876 (C–H), 1614, 1496, 1462, 1416 cm^{-1} (C=C, C=N). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.06 {18H, s, CH[Si(CH_3)$_3$]$_2$}, 3.55 {1H, s, CH[Si(CH_3)$_3$]$_2$}, 7.04–7.09 (1H, m, ArH), 7.29–7.30 (2H, m, ArH), 7.69 (1H, d, J 8.1, ArH), 7.94 (1H, s, 3-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ −0.45 {CH[Si(*C*H$_3$)$_3$]$_2$}, 43.09 {*C*H[Si(CH$_3$)$_3$]$_2$}, 109.37 (Ar:C7), 119.54, 120.80, 125.13 (Ar:C4–C6), 131.22 (Ar:C3), 123.14 (Ar:C3a), 139.86 (Ar:C7a). m/z (EI): 276 (M^+, 26%), 261 ($M^+ - Me$, 21%), 203 ($M^+ - SiMe_3$, 70%), 73 ($SiMe_3^+$, 100%) (HRMS Found: MH^+, 277.154870; $C_{14}H_{24}N_2Si_2$. Calc.: MH^+, 277.155631).

4.8. 2-[bis(Trimethylsilyl)methyl]-3-trimethylsilylindazole (4)

A solution of 2-methylindazole (**13**) (481 mg, 3.64 mmol) in THF (20 ml) was treated with t-BuLi (7.7 ml, 12.78 mmol) and TMSCl (1.85 ml, 14.58 mmol) according to the procedure in Section 4.7 to afford an orange oil. Column chromatography (petrol–ether (19:1)) gave compound **4** (1.25 g, 98%) as a colourless oil. IR ν_{max} (film): 3090, 3046 (C–H)Ar, 2955, 2900 (C–H), 1617, 1579, 1544, 1489, 1450 cm^{-1} (C=C, C=N). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.08 {18H, s, CH[Si(CH_3)$_3$]$_2$}, 0.50 [9H, s, Si(CH_3)$_3$], 3.74 {1H, s, CH[Si(CH$_3$)$_3$]$_2$}, 7.02 (1H, m, ArH), 7.21 (1H, m, ArH), 7.71 (1H, d, J 9.3, ArH), 7.74 (1H, d, J 9.0, ArH). ^{13}C-NMR (125 MHz, $CDCl_3$): δ −0.68 {CH[Si(*C*H$_3$)$_3$]$_2$}, 1.14 [Si(*C*H$_3$)$_3$], 49.49 {*C*H[Si(CH$_3$)$_3$]$_2$}, 117.26, 120.19, 120.66, 123.70 (Ar:C4–C7), 129.32 (Ar:C3a), 132.84 (Ar:C3), 148.85 (Ar:C7a). m/z (EI): 348 (M^+, 30%), 333 ($M^+ - Me$, 85%), 275 ($M^+ - SiMe_3$, 69%), 73 ($SiMe_3$, 100%) (HRMS Found: MH^+, 349.195256; $C_{17}H_{32}N_2Si_3$. Calc.: MH^+, 349.195160).

4.9. {η^6-1-[bis(Trimethylsilyl)methyl]indazole}tricarbonylchromium (14)

A mixture of compound **3** (758 mg, 2.75 mmol) and $Cr(CO)_6$ (1.00 g, 4.55 mmol) in Bu_2O (50 ml) and n-heptane (50 ml) was heated at reflux for 6 days. The solution was treated as in procedure of Section 4.4 to afford a red oil. Column chromatography [petrol–ether (9:1)], followed by recrystallisation from ether–n-hexane, gave complex **14** (678 mg, 60%) as orange crystals. M.p. (dec.) 155°C. IR ν_{max} (KBr): 3090 (C–H)Ar, 2956, 2901 (C–H), 1948, 1880, 1858 (C≡O), 1555, 1515, 1465, 1446, 1429, 1402 cm^{-1} (C=C, C=N). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.03 [9H, s, CHSi(CH_3)$_3$], 0.17 [9H, s, CHSi(CH_3)$_3$], 3.35 {1H, s, CH[Si(CH$_3$)$_3$]$_2$}, 5.28 (1H, t, J 6.6, 5-H or 6-H), 5.37 (1H, t, J 6.6, 6-H or 5-H), 6.00 (1H, d, J 6.6, 4-H or 7-H), 6.23 (1H, d, J 6.6, 7-H or 4-H), 7.85 (1H, s, 3-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ −0.52 [CHSi(*C*H$_3$)$_3$], 0.05 [CHSi(*C*H$_3$)$_3$], 44.01 {*C*H[Si(CH$_3$)$_3$]$_2$}, 76.59 (Ar:C7), 84.86, 89.17, 90.15 (Ar:C4–C6), 94.11 (Ar:C3a), 118.38 (Ar:C7a), 134.23 (Ar:C3), 232.60 (*C*O). m/z (APCI$^+$): 413 (MH^+, 18%), 357 ($MH^+ - 2CO$, 20%), 329 ($MH^+ - 3CO$, 27%), 277 [$MH^+ - Cr(CO)_3$, 100%]. Anal. Found: C, 49.52; H, 5.65; N, 6.60. Calc.: C, 49.49; H, 5.86; N, 6.79%.

4.10. {η^6-2-[bis(Trimethylsilyl)methyl]-3-trimethylsilylindazole}tricarbonylchromium (15)

A mixture of compound **4** (1.61 g, 4.61 mmol) and $Cr(CO)_6$ (1.52 g, 6.92 mmol) in Bu_2O (50 ml) and n-heptane (50 ml) was heated at reflux for 6 days. The solution was treated as in procedure of Section 4.4 to afford a red oil. Recrystallisation from ether–petrol gave compound **15** (2.05 g, 92%) as red crystals. M.p. 169–170°C. IR ν_{max} (KBr): 2958, 2901 (C–H), 1958, 1875, 1860 (C≡O), 1554, 1494, 1437 cm^{-1} (C=C, C=N). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.05 [9H, s, CHSi(CH_3)$_3$], 0.12 [9H, s, CHSi(CH_3)$_3$], 0.54 [9H, s, Si(CH_3)$_3$], 3.66 {1H, s, CH[Si(CH$_3$)$_3$]$_2$}, 5.29 (1H, t, J 6.7, 5-H or 6-H), 5.51 (1H, t, J 6.7, 6-H or 5-H), 6.34 (1H, d, J 6.8, 4-H or 7-H), 6.47 (1H, d, J 6.9, 7-H or 4-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ −0.84 [CHSi(*C*H$_3$)$_3$], −0.45 [CHSi(*C*H$_3$)$_3$], 0.61 [Si(*C*H$_3$)$_3$], 52.15 {*C*H[Si(CH$_3$)$_3$]$_2$}, 82.49, 85.03, 89.30, 92.34 (Ar:C4–C7), 103.47 (Ar:C3a), 126.88 (Ar:C7a), 138.21 (Ar:C3), 233.55 (*C*O). m/z (EI): 484 (M^+, 1%), 400 ($M^+ - 3CO$, 10%), 348 [$M^+ - Cr(CO)_3$, 10%], 333 (348-Me, 21%), 275 (348-$SiMe_3$, 34%), 73 ($SiMe_3^+$, 100%). Anal. Found: C, 49.78; H, 6.75; N, 5.76. Calc.: C, 49.56; H, 6.65; N, 5.78%.

4.11. {η^6-1-[bis(Trimethylsilyl)methyl]-4-methylindazole}tricarbonylchromium (16), {η^6-1-[1′,1′-bis(trimethylsilyl)ethyl]-4-methylindazole}tricarbonylchromium (17) and {η^6-1-[bis(trimethylsilyl)methyl]-7-methylindazole}tricarbonylchromium (18)

4.11.1. Reaction of complex 14 with n-BuLi–TMEDA and MeI

n-BuLi (0.23 ml, 0.315 mmol) was added dropwise to a solution of complex **14** (100 mg, 0.242 mmol) and TMEDA (0.11 ml, 0.726 mmol) in THF (20 ml), at −78°C. After stirring at −78°C for 1.5 h, MeI (0.05 ml, 0.726 mmol) was added. The solution was stirred at −78°C for 3 h and subsequently was allowed to warm slowly to r.t. and stirred overnight. Work-up was performed using the same procedure as in Section 4.6.1 to afford a red oil. Column chromatography [n-hexane–CH_2Cl_2 (10:1)] led to the isolation of two fractions. Recrystallisation of the first fraction from petrol gave complex **17** (12 mg, 11%) as orange crystals. Repeated recrystallisation of the second fraction from petrol gave complex **16** (25 mg, 24%) as orange crystals, with the

mother liquors enriched in complex **18**. Complex **16**: M.p. (dec.) 164–165°C. IR ν_{max} (KBr): 2958, 2359 (C–H), 1951, 1860 (C≡O), 1547, 1470, 1434 cm^{-1} (C=C, C=N). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.04 [9H, s, $CHSi(CH_3)_3$], 0.18 [9H, s, $CHSi(CH_3)_3$], 2.63 (3H, s, CH_3), 3.36 {1H, s, $CH[Si(CH_3)_3]_2$}, 5.12 (1H, d, *J* 5.9, 5-H), 5.41 (1H, t, *J* 6.6, 6-H), 5.87 (1H, d, *J* 6.9, 7-H), 7.90 (1H, s, 3-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ −0.44 [$CHSi(CH_3)_3$], 0.15 [$CHSi(CH_3)_3$], 18.39 (CH_3), 44.10 {$CH[Si(CH_3)_3]_2$}, 74.71 (Ar:C7), 89.47, 90.75 (Ar:C5,C6), 95.98 (Ar:C4), 101.51 (Ar:C3a), 119.13 (Ar:C7a), 133.46 (Ar:C3), 232.90 (*C*O). *m*/*z* (CI/NH_3): 427 (MH^+, 9%), 291 [MH^+–$Cr(CO)_3$, 100%]. Anal. Found: C, 50.67; H, 6.00; N, 6.51. Calc.: C, 50.68; H, 6.14; N, 6.57%.

Complex **17**: M.p. (dec.) 146°C. IR ν_{max} (KBr): 2973 (C–H), 1947, 1877, 1856 (C≡O), 1541, 1468, 1438 cm^{-1} (C=C, C=N). ^{1}H-NMR (200 MHz, $CDCl_3$): δ −0.03 [9H, s, $C(Me)Si(CH_3)_3$], 0.19 [9H, s, $C(Me)Si(CH_3)_3$], 2.04 [3H, s, $C(CH_3)Si(CH_3)_3$], 2.63 (3H, s, CH_3), 5.00 (1H, d, *J* 5.9, 5-H or 7-H), 5.44 (1H, t, *J* 7.0, 6-H), 6.20 (1H, d, *J* 7.2, 7-H or 5-H), 7.86 (1H, s, 3-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ −1.21 [$C(Me)Si(CH_3)_3$], 0.32 [$C(Me)Si(CH_3)_3$], 16.28 (CH_3), 18.52 (CH_3), 51.40 [$C(Me)(SiMe_3)_2$], 76.45 (Ar:C7), 88.27, 92.16 (Ar:C5,C6), 95.60 (Ar:C4), 102.45 (Ar:C3a), 121.75 (Ar:C7a), 133.07 (Ar:C3), 233.06 (*C*O). *m*/*z* ($APCI^+$): 441 (MH^+, 10%), 413 (MH^+–CO, 6%), 305 [MH^+–$Cr(CO)_3$, 7%] (HRMS Found: MH^+, 441.113437; $C_{19}H_{28}CrN_2O_3Si_2$. Calc.: MH^+, 441.112185). ^{1}H-NMR spectrum of complex **18** in the mixture: ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.08 [9H, s, $CHSi(CH_3)_3$], 0.20 [9H, s, $CHSi(CH_3)_3$], 2.80 (3H, s, CH_3), 3.86 {1H, s, $CH[Si(CH_3)_3]_2$}, 5.11 (1H, d, *J* 5.6, 4-H or 6-H), 5.29 (1H, t, *J* 6.1, 5-H), 6.09 (1H, d, *J* 5.9, 6-H or 4-H), 7.88 (1H, s, 3-H).

*4.11.2. Reaction of complex **14** with n-BuLi and MeI*

A solution of complex **14** (60 mg, 0.145 mmol) in THF (10 ml) was treated with *n*-BuLi (0.14 ml, 0.189 mmol) and MeI (0.03 ml, 0.435 mmol) according to the procedure in Section 4.11.1 to afford a red oil. Column chromatography [*n*-hexane–CH_2Cl_2 (10:1)], followed by a series of recrystallisations from petrol, gave complex **16** (19 mg, 31%) as orange crystals. The mother-liquors were enriched in complex **18**.

*4.12. {η^6-2-[bis(Trimethylsilyl)methyl]-7-methyl-3-trimethylsilylindazole}tricarbonylchromium (**5**)*

A solution of complex **15** (139 mg, 0.287 mmol) and TMEDA (0.13 ml, 0.861 mmol) in THF (20 ml) was treated with *n*-BuLi (0.27 ml, 0.373 mmol) and MeI (0.05 ml, 0.861 mmol) according to the procedure in Section 4.11.1 to afford a red oil. Column chromatography [*n*-hexane–CH_2Cl_2 (10:1)], followed by recrystallisation from ether–*n*-hexane, gave complex **5** (99 mg, 81%) as red crystals. M.p. (dec.) 147–148°C. IR ν_{max} (KBr): 2960, 2917, 2849 (C–H), 1946, 1875, 1858 (C≡O), 1567, 1539, 1463, 1422 cm^{-1} (C=C, C=N). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.07 [9H, s, $CHSi(CH_3)_3$], 0.13 [9H, s, $CHSi(CH_3)_3$], 0.53 [9H s, $Si(CH_3)_3$], 2.67 (3H, s, CH_3), 3.66 {1H, s, $CH[Si(CH_3)_3]_2$}, 5.28 (1H, t, *J* 6.4, 5-H), 5.38 (1H, d, *J* 5.9, 6-H), 6.20 (1H, d, *J* 6.6, 4-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ −0.79 [$CHSi(CH_3)_3$], −0.40 [$CHSi(CH_3)_3$], 0.57 [$Si(CH_3)_3$], 16.94 (CH_3), 52.24 {$CH[Si(CH_3)_3]_2$}, 83.61, 89.59, 92.83 (Ar:C4–C6), 98.90 (Ar:C7), 103.58 (Ar:C3a), 128.08 (Ar:C7a), 138.14 (Ar:C3), 234.01 (*C*O). *m*/*z* ($APCI^+$): 499 (MH^+, 100%), 363 [MH^+–$Cr(CO)_3$, 39%]. Anal. Found: C, 50.31; H, 7.02; N, 5.72. Calc.: C, 50.57; H, 6.87; N, 5.62%.

*4.13. {η^6-2-[bis(Trimethylsilyl)methyl]-7-methoxycarbonyl-3-trimethylsilylindazole}-tricarbonylchromium (**19**) and 2-[bis(trimethylsilyl)methyl]-7-methoxycarbonyl-3-trimethylsilylindazole (**21**)*

A solution of complex **15** (122 mg, 0.253 mmol) and TMEDA (0.11 ml, 0.759) in THF (20 ml) was treated with *n*-BuLi (0.23 ml, 0.323 mmol) and $ClCO_2Me$ (0.06 ml, 0.759 mmol) according to the procedure in Section 4.11.1 to afford an orange oil. Column chromatography [*n*-hexane–ether (10:1)], followed by recrystallisation from petrol, gave complex **19** (34 mg, 25%) as brown crystals and compound **21** (34 mg, 33%) as white crystals. Complex **19**: M.p. (dec.) 121–122°C. IR ν_{max} (KBr): 2958, 2903 (C–H), 1951, 1894, 1871 (C≡O), 1715 (C=O), 1633, 1539, 1501, 1435 cm^{-1} (C=C, C=N). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.05 [9H, s, $CHSi(CH_3)_3$], 0.14 [9H, s, $CHSi(CH_3)_3$], 0.55 [9H s, $Si(CH_3)_3$], 3.66 {1H, s, $CH[Si(CH_3)_3]_2$}, 4.03 (3H, s, CO_2CH_3), 5.29 (1H, t, *J* 6.6, 5-H), 6.38 (1H, d, *J* 6.3, 4-H or 6-H), 6.50 (1H, d, *J* 6.7, 6-H or 4-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ −0.91 [$CHSi(CH_3)_3$], −0.57 [$CHSi(CH_3)_3$], 0.59 [$Si(CH_3)_3$], 52.33, 52.51 [$CH(Si(CH_3)_3)_2$, CO_2CH_3], 80.72 (Ar:C7), 86.91, 87.39, 94.66 (Ar:C4–C6), 101.55 (Ar:C3a), 126.03 (Ar:C7a), 139.00 (Ar:C3), 167.56 (CO_2Me), 232.14 (*C*O). *m*/*z* (CI/NH_3): 543 (MH^+, 62%), 407 [MH^+–$Cr(CO)_3$, 100%] (HRMS Found: MH^+, 543.125209; $C_{22}H_{34}N_2Si_3CrO_5$. Calc.: MH^+, 543.125893). Compound **21**: M.p. 49–50°C. IR ν_{max} (KBr): 2957, 2902 (C–H), 1712 (C=O), 1606, 1553, 1436 cm^{-1} (C=C, C=N). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.10 {18H, s, $CH[Si(CH_3)_3]_2$}, 0.52 [9H, s, $Si(CH_3)_3$], 3.74 {1H, s, $CH[Si(CH_3)_3]_2$}, 4.00 (3H, s, CO_2CH_3), 7.09 (1H, t, *J* 8.4, 5-H), 7.95–8.03 (2H, m, 4-H and 6-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ −0.78 {$CH[Si(CH_3)_3]_2$}, 1.09 [$Si(CH_3)_3$], 50.20 {$CH[Si(CH_3)_3]_2$}, 51.59 (CO_2CH_3), 118.84 (Ar:C7), 119.38, 126.20, 128.53 (Ar:C4–C6), 130.95, 135.46 (Ar:C3,C3a), 145.97 (Ar:C7a), 167.95

(CO_2Me). m/z ($APCI^+$): 407 (MH^+, 100%) (HRMS Found: MH^+, 407.201594; $C_{19}H_{34}N_2O_2Si_3$. Calc.: MH^+, 407.200639).

4.14. {η⁶-2-[bis(Trimethylsilyl)methyl]-7-etoxycarbonyl-3-trimethylsilylindazole}tricarbonyl–chromium (20) and 2-[bis(trimethylsilyl)methyl]-7-etoxycarbonyl-3-trimethylsilylindazole (22)

A solution of complex **15** (116 mg, 0.240 mmol) and TMEDA (0.10 ml, 0.720 mmol) in THF (20 ml) was treated with *n*-BuLi (0.22 ml, 0.312 mmol) and $ClCO_2Et$ (0.07 ml, 0.720 mmol) according to the procedure in Section 4.11.1 to afford a red–brown oil. Column chromatography [*n*-hexane–ether (10:1)], followed by recrystallisation from petrol, gave complex **20** (34 mg, 26%) as red–brown crystals and compound **22** (40 mg, 40%) as white crystals. Complex **20**: M.p. (dec.) 146–147°C. IR ν_{max} (KBr): 2958, 2903 (C–H), 1960, 1896, 1865 (C≡O), 1708 (C=O), 1636, 1541, 1502, 1438 cm^{-1} (C=C, C=N). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.06 [9H, s, $CHSi(CH_3)_3$], 0.14 [9H, s, $CHSi(CH_3)_3$], 0.55 [9H s, $Si(CH_3)_3$], 1.46 (3H, t, J 7.2, $CO_2CH_2CH_3$), 3.68 {1H, s, $CH[Si(CH_3)_3]_2$}, 4.43–4.60 (2H, m, $CO_2CH_2CH_3$), 5.30 (1H, t, J 6.6, 5-H), 6.40 (1H, d, J 6.4, 4-H or 6-H), 6.50 (1H, d, J 6.8, 6-H or 4-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ −0.86 [$CHSi(CH_3)_3$], −0.51 [$CHSi(CH_3)_3$], 0.67 [$Si(CH_3)_3$], 14.62 ($CO_2CH_2CH_3$), 52.50 {$CH[Si(CH_3)_3]_2$}, 61.62 ($CO_2CH_2CH_3$), 81.12 (Ar:C7), 86.85, 87.42, 94.88 (Ar:C4–C6), 101.80 (Ar:C3a), 126.00 (Ar:C7a), 139.00 (Ar:C3), 167.26 (CO_2Et), 232.19 (CO). m/z ($APCI^+$): 557 (MH^+, 97%), 421 [MH^+–$Cr(CO)_3$, 100%]. Anal. Found: C, 49.56; H, 6.54; N, 4.89. Calc.: C, 49.61; H, 6.52; N, 5.03%. Compound **22**: M.p. 97–98°C. IR ν_{max} (KBr): 2956, 2903 (C–H), 1701 (C=O), 1606, 1552, 1479, 1457 cm^{-1} (C=C, C=N). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.09 {18H, s, $CH[Si(CH_3)_3]_2$}, 0.51 [9H s, $Si(CH_3)_3$], 1.45 (3H, t, J 7.1, $CO_2CH_2CH_3$), 3.74 {1H, s, $CH[Si(CH_3)_3]_2$}, 4.46 (2H, q, J 7.1, $CO_2CH_2CH_3$), 7.08 (1H, t, J 8.1, 5-H), 7.94 (1H, d, J 8.2, 4-H or 6-H), 8.01 (1H, d, J 7.1, 6-H or 4-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ −0.30 {$CH[Si(CH_3)_3]_2$}, 1.57 [$Si(CH_3)_3$], 15.08 ($CO_2CH_2CH_3$), 50.57 {$CH[Si(CH_3)_3]_2$}, 61.08 ($CO_2CH_2CH_3$), 119.64 (Ar:C7), 119.83, 126.51, 129.16 (Ar:C4–C6), 131.44, 133.95 (Ar:C3,C3a), 146.41 (Ar:C7a), 167.98 (CO_2Et). m/z ($APCI^+$): 421 (MH^+, 100%). Anal. Found: C, 57.23; H, 8.81; N, 6.50. Calc.: C, 57.09; H, 8.62; N, 6.66%).

4.15. 1-[bis(Trimethylsilyl)methyl]-4-methylindazole (23)

A solution of complex **16** (10 mg, 0.023 mmol) in ether (10 ml) was exposed to air and sunlight. After 6 days, filtration through Celite® and evaporation of the solvent gave colourless oil. Column chromatography [petrol–ether (10:1)] gave compound **23** (5 mg, 75%) as white crystals. M.p. 52–53°C. IR ν_{max} (KBr): 3048 (C–H)Ar, 2958, 2901, 2877, 2857 (C–H), 1605, 1586, 1505, 1459, 1416 cm^{-1} (C=C, C=N). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.06 {18H, s, $CH[Si(CH_3)_3]_2$}, 2.59 (3H, s, CH_3), 3.54 {1H, s, $CH[Si(CH_3)_3]_2$}, 6.84 (1H, d, J 6.6, ArH), 7.13–7.25 (2H, m, ArH), 7.95 (1H, s, 3-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ −0.47 {$CH[Si(CH_3)_3]_2$}, 18.60 (CH_3), 43.15 {$CH[Si(CH_3)_3]_2$}, 106.95 (Ar:C7), 119.54, 125.27 (Ar:C5, C6), 123.61, 124.02 (Ar:C4,C3a), 130.03 (Ar:C3), 139.78 (Ar:C7a). m/z ($APCI^+$): 291 (MH^+, 100%) (HRMS Found: MH^+, 291.170450; $C_{15}H_{26}N_2Si_2$. Calc.: MH^+, 291.171281).

4.16. 2-[bis(Trimethylsilyl)methyl]-7-methyl-3-trimethylsilylindazole (24)

A solution of complex **5** (53 mg, 0.106 mmol) in ether (20 ml) was exposed to air and sunlight. After 10 days, filtration through Celite® and evaporation of the solvent gave a pale yellow oil. Column chromatography [petrol–ether (10:1)] gave compound **24** (29 mg, 76%) as a colourless oil. IR ν_{max} (film): 3045 (C–H)Ar, 2956, 2900 (C–H), 1567 cm^{-1} (C=C, C=N). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.08 {18H, s, $CH[Si(CH_3)_3]_2$}, 0.49 [9H, s, $Si(CH_3)_3$], 2.59 (3H, s, CH_3), 3.71 {1H, s, $CH[Si(CH_3)_3]_2$}, 6.89–6.96 (2H, m, ArH), 7.54–7.59 (1H, m, ArH). ^{13}C-NMR (125 MHz, $CDCl_3$): δ −0.69 {$CH[Si(CH_3)_3]_2$}, 1.08 [$Si(CH_3)_3$], 17.09 (CH_3), 49.43 {$CH[Si(CH_3)_3]_2$}, 118.09, 120.44, 122.72 (Ar:C5–C7), 127.41, 128.87 (Ar:C7, C3a), 132.80 (Ar:C3), 148.83 (Ar:C7a). m/z ($APCI^+$): 363 (MH^+, 100%) (HRMS Found: MH^+, 363.212280; $C_{18}H_{34}N_2Si_3$. Calc.: MH^+, 363.210810).

4.17. Crystal structure determination of complex (5)

4.17.1. Crystal data

$C_{42}H_{68}Cr_2N_4O_6Si_6$, $M = 997.54$. Data was collected at r.t. Triclinic, with cell dimensions $a = 9.995(2)$, $b = 15.982(3)$, $c = 17.651(4)$ Å, $\alpha = 81.11(2)$, $\beta = 75.03(2)$ and $\gamma = 82.52(2)°$, space group P-1, $V = 2679(1)$ Å^3, $Z = 2$ (with two molecules in the asymmetric unit), $d_{calc} = 1.237$ g cm^{-3}, $\mu = 0.534$ mm^{-1}, $F(000) = 1056$. 10130 reflections were collected from which 8987 were independent ($R_{int} = 0.0350$) and used in the structure refinement. Two molecules were found in the asymmetric unit. Final R values are: R_1 [$I > 2\sigma(I)$] = 0.0700, wR_2 [$I > 2\sigma(I)$] = 0.1828, R_1 (all data) = 0.1167, wR_2 (all data) = 0.2161.

5. Supplementary material

Full details of data collection and refinement, tables of final atomic coordinates, anisotropic thermal parameters for all non-hydrogen atoms, hydrogen atomic coordinates, complete tables for bond lengths and angles as well as torsion angles have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 141004 for complex **5**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax.: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank Fundação para a Ciência e a Tecnologia (Programa Praxis XXI) for provision of funding (to F.C.T.).

References

[1] J. Elguero, in: A.R. Katritzky, C.W. Rees (Eds.), Comprehensive Heterocyclic Chemistry, vol. 5, Pergamon, Oxford, 1984, pp. 167–303.
[2] J. Elguero, in: A.R. Katritzky, C.W. Rees, E.F.V. Scriven (Eds.), Comprehensive Heterocyclic Chemistry II, vol. 3, Pergamon, Oxford, 1996, pp. 1–75.
[3] J. Elguero, A. Fruchier, E.M. Tjiou, S. Trofimenko, Khim. Geterotsikl. Soedin. 9 (1995) 1159 and references therein.
[4] (a) Atta-ur-Rahman, S. Malik, H. Cun-Heng, J. Clardy, Tetrahedron Lett. 26 (1985) 2759. (b) Atta-ur-Rahman, S. Malik, S.S. Hasan, M.I. Choudhary, C.Z. Ni, J. Clardy, Tetrahedron Lett. 36 (1995) 1993.
[5] M.R. Grimmett, in: D. Barton, W.D. Ollis (Eds.), Comprehensive Organic Chemistry, vol. 5, Pergamon, Oxford, 1979, pp. 357–410.
[6] (a) G. Corsi, G. Palazzo, C. Germani, P.S. Barcellona, B. Silvestrini, J. Med. Chem. 19 (1976) 778 and references there in. (b) Y. Ikeda, N. Takano, H. Matsushita, Y. Shiraki, T. Koide, R. Nagashima, Y. Fujimura, M. Shindo, S. Suzuki, T. Iwasaki, Arzneim. Forsch. Drug. Res. 29 (1979) 511. (c) S. Tono-oka, I. Sekikawa, I. Azuma, Chem. Lett. (1983) 805. (d) S. Tono-oka, Y. Tone, V.E. Marquez, D.A. Cooney, I. Sekikawa, I. Azuma, Bull. Chem. Soc. Jpn. 58 (1985) 307 (e) J. Guillaume, C. Dumond, L. Nedelec, Eur. J. Med. 22 (1987) 23. (f) F. Gatta, M. Luciani, G. Palazzo, J. Heterocyclic. Chem. 26 (1989) 613. (g) F. Seela and W. Bourgeois, Helv. Chim. Acta 74 (1991) 315. (h) W.M. Welch, C.E. Hanau, W.M. Whalen, Synthesis (1992) 937. (i) J. Catalán, J.C. Valle, R.M. Claramunt, G. Boyer, J. Laynez, J. Gómez, P. Jiménez, F. Tomás and J. Elguero, J. Phys. Chem. 41 (1994) 10606. (j) V.J. Arán, M. Flores, P. Muñoz, J.R. Ruiz, P. Sánchez-Verdú, M. Stud, Liebigs Ann. (1995) 817. (l) J. Catalán, J.L.G. Paz, J. Elguero, J. Chem. Soc. Perkin Trans. 2 (1996) 57. (m) T. Yoshida, N. Matsuura, K. Yamamoto, M. Doi, K. Shimada, T. Morie, S. Kato, Heterocyclic 43 (1996) 2701. (n) S. Budavari (Ed.), The Merck Index, 12th edn., Merck, Rahway, NJ, 1996. (o) J.H. Sun, C.A. Teleha, J.S. Yan, J.D. Rodgers, D.A. Nugiel, J. Org. Chem. 62 (1997) 5627. (p) A.P. Krapcho, S.N. Haydar, J. Heterocyclic. Chem. 34 (1997) 1637. (q) T. Morie, H. Harada, S. Kato, Synth. Commun. 27 (1997) 559. (r) H. Harada, T. Morie, Y. Hirokawa, S. Kato, Tetrahedron Asymm. 8 (1997) 2367.
[7] (a) H.D. Porter, W.D. Peterson, in: E.C. Horning (Ed.), Organic Synthesis, Coll. vol. 3, Wiley, NY, 1955, p. 660. (b) C. Ainsworth, J. Am. Chem. Soc. 79 (1957) 5242. (c) C. Ainsworth, in: M. Tishler (Ed.), Organic Synthesis, vol. 39, Wiley, NY, 1959, p. 27. (d) L. Krbechek, H. Takimoto, J. Org. Chem. 29 (1964) 1150. (e) W.A.F. Gladstone and R.O.C. Norman, J. Chem. Soc. (1965) 3048. (f) J.I.G. Cadogan, M. Cameron-Wood, R.K. Mackie, R.J.G. Searle, J. Chem. Soc. (1965) 4831. (g) M. Armour, J.I.G. Cadogan, D.S.B. Grace, J. Chem. Soc. Perkin Trans. 1 (1975) 1185. (h) J.M. Bakke and K.A. Skjervold, Acta Chem. Scand. B 29 (1975) 1089. (i) L. Baiocchi, G. Corsi, G. Palazzo, Synthesis (1978) 633. (j) C. Wentrup, A. Damerius, W. Reichen, J. Org. Chem. 43 (1978) 2037. (l) M.A. Ardakani, R.K. Smalley, R.H. Smith, Synthesis (1979) 308. (m) C. Rüchardt, V. Hassmann, Liebigs Ann. Chem. (1980) 908. (n) R.A. Bartsch, I. Yang, J. Heterocyclic. Chem. 21 (1984) 1063. (o) M. Akazome, T. Kondo, Y. Watanabe, J. Chem. Soc., Chem. Commun. (1991) 1466. (p) C. Dell′Erba, M. Novi, G. Petrillo, C. Tavani, Tetrahedron 48 (1992) 325. (q) Z. Zhenqi, X. Tongsheng, C. Xiaonai, Q. Yuzhu, Z. Zheng and H. Hogwen, J. Chem. Soc. Perkin Trans. 1 (1993) 1279 and references therein. (r) C. Dell′Erba, M. Novi, G. Petrillo, C. Tavani, Tetrahedron 50 (1994) 3529. (s) M. Akazome, T. Kondo, Y. Watanabe, J. Org. Chem. 59 (1994) 3375. (t) F. Halley, X. Sava, Synth. Commun. 27 (1997) 1199. (u) B.A. Frontana-Uribe, C. Moinet, Tetrahedron 54 (1998) 3197.
[8] R. Usón, L.A. Oro, M.A. Ciriano, M.C. Bello, J. Organomet. Chem. 240 (1982) 199.
[9] J.R. Shapley, D.E. Samkoff, C. Bueno, M.R. Churchill, Inorg. Chem. 21 (1982) 634.
[10] J.A. Cabeza, C. Landazuri, L.A. Oro, A. Tiripicchio, M. Tiripicchio-Camellini, J. Organomet. Chem. 322 (1987) C16.
[11] D. Carmona, J. Ferrer, L.A. Oro, M.C. Apreda, C. Foces-Foces, F.H. Cano, J. Elguero, J.L. Jimeno, J. Chem. Soc. Dalton Trans. (1990) 1463.
[12] A.J. Deeming, C. Whittaker, A.J. Arce, Y. De Sanctis, J. Organomet. Chem. 540 (1997) 67.
[13] A. Boo, B.S. Casas, U. Casellato, M.D. Couce, E. Freijanes, R. Graziani, B. Salgado, U. Russo, J. Sordo, J. Organomet. Chem. 530 (1997) 141.
[14] A.L. Rheingold, B.S. Haggerty, G.P.A. Yap, S. Trofimenko, Inorg. Chem. 36 (1997) 5097.
[15] E.O. Fischer, K. Öfele, Chem. Ber. 91 (1958) 2395.
[16] (a) R. Davis, L.A.P. Kane-Maguire, in: G. Wilkinson, F.G.A. Stone and E.W. Abel (Ed.), Comprehensive Organometallic Chemistry, vol. 3, Pergamon, Oxford, 1982, p. 1001–1051, see p.1016. (b) E.O Fischer, H.A. Goodwin, C.G. Kreiter, H.D. Simmons Jr., K. Sonogashira, S.B. Wild, J. Organomet. Chem. 14 (1968) 359.
[17] (a) A. Goti, M.F. Semmelhack, J. Organomet. Chem. 470 (1994) C4. (b) R. Wolfgramm, S. Laschat, J. Organomet. Chem. 575 (1999) 141.
[18] M. Prokesová, S. Toma, Chem. Pap. 47 (1993) 314.
[19] J.P. Selegue, K.A. Swarat, J. Am. Chem. Soc. 115 (1993) 6448.
[20] S.G. Davies, M.R. Shipton, J. Chem. Soc. Chem. Commun. (1989) 995.
[21] S.G. Davies, M.R. Shipton, J. Chem. Soc. Perkin Trans. 1 (1991) 501.
[22] M.S. Loft, T.J. Mowlem, D.A. Widdowson, D.J. Williams, J. Chem. Soc. Perkin Trans. 1 (1995) 105.
[23] A. Solladié-Cavallo, M. Bencheqroun, J. Organomet. Chem. 403 (1991) 159.
[24] P.J. Sheldrake, D. Phil Thesis, University of Oxford, Oxford, 1994.

[25] J. Elguero, A. Fruchier, R. Jacquier, Bull. Soc. Chim. Fr. (1966) 2075.
[26] J. Elguero, A. Fruchier, R. Jacquier, U. Scheidegger, J. Chim. Phys. Phys. Chim. Biol. 68 (1971) 1113.
[27] M.H. Palmer, R.H. Findlay, S.M.F. Kennedy, P.S. McIntyre, J. Chem. Soc. Perkin Trans. 2 (1975) 1695.
[28] P. Bouchet, A. Fruchier, G. Joncheray, J. Elguero, Org. Magn. Reson. 9 (1977) 716.
[29] M. Begtrup, R.M. Claramunt, J. Elguero, J. Chem. Soc. Perkin Trans. 2 (1978) 99.
[30] L. Stefaniak, Org. Magn. Reson. 11 (1978) 385.
[31] B.A. Tertov, P.P. Onishchenko, Chem. Heterocycl. Compd. (1970) 1339.
[32] M. Kamiya, Bull. Chem. Soc. Jpn. 43 (1970) 3344.
[33] G. Nechvatal, D.A. Widdowson, D.J. Williams, J. Chem. Soc. Chem. Commun. (1981) 1260.
[34] T.A. Albright, B.K. Carpenter, Inorg. Chem. 19 (1980) 3092.
[35] P.D. Baird, J. Blagg, S.G. Davies, K.H. Sutton, Tetrahedron 44 (1988) 171.
[36] D.D. Perrin, W.L.F. Armarego, D.R. Perrin, Purification of Laboratory Chemicals, 2nd, Pergamon, Oxford, 1980.