Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 691 (2006) 846–858
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Synthesis of *syn*-facial (Cr,Mn) benzyl complexes by the stereoselective thermolytic coupling of unsymmetric diazomethanes with cyclomanganated (η^6-arene)tricarbonylchromium complexes

Jean-Pierre Djukic [a,*], Christophe Michon [a], Alexsandro Berger [a], Michel Pfeffer [a], André de Cian [b,1], Nathalie Kyritsakas-Gruber [b]

[a] *Laboratoire de Synthèses Métallo-induites, Centre National de la Recherche Scientifique, UMR 7513 CNRS, Université Louis Pasteur, 4, rue Blaise Pascal, 67070 Strasbourg Cedex, France*
[b] *Service de Détermination Structurale par Diffraction des Rayons X, UMR 7513 CNRS, Université Louis Pasteur, 4, rue Blaise Pascal, 67070 Strasbourg Cedex, France*

Received 27 July 2005; received in revised form 11 October 2005; accepted 21 October 2005
Available online 5 December 2005

Abstract

The heat-promoted reaction of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene with cyclomanganated 2-[tricarbonyl(η^6-phenyl)chromium]pyridine afforded, upon departure of a molecule of CO, a new stable manganese alkylidene complex in which, according to X-ray diffraction analyses, the heterocyclic ligand is *anti*-facial with respect to the $Cr(CO)_3$ moiety. Similar heat-promoted reactions of unsymmetrically substituted diazoalkanes such as $(Me_3Si)(H)CN_2$, $(Ph)(Me)CN_2$, $(Ph)(t\text{-}Bu)CN_2$ and $(Ph)(FcCH_2CH_2)CN_2$, which are precursors of more electrophilic alkylidenes, with cyclomanganated 2-[tricarbonyl(η^6-phenyl)chromium]pyridine derivatives afforded new *syn*-facial heterobimetallic benzyl complexes. The stereoselectivity of these reactions depends on the steric demand of the substituents at the diazoalkane. A phenyl substituent at the diazoalkane favors the formation of *syn*-facial heterobimetallic benzyl complexes with the Ph group in the *endo* position. Combining this "phenyl directing effect" to the steric effect operated by a bulky group at the phenyldiazoalkane, like noticed with $(Ph)(t\text{-}Bu)CN_2$, led to total stereoselectivity. This study discloses four new X-ray structures of *syn*-facial Cr,Mn benzyl complexes, which all present the same short Cr-to-Mn distance of ca. 3.04 Å.

Keywords: Chromium; Manganese; Diazoalkane; Insertion; X-ray diffraction; Metallacycles

1. Introduction

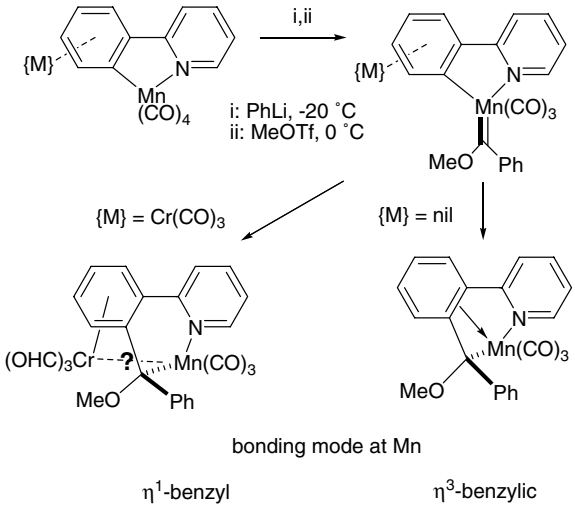
Intermetallic interactions in so-called d-block heterobimetallic transition metal complexes depend on the nature of the retinue of ligands and on the type of bonding the latter establish with the metallic centers. In face-sharing, so-called *syn*-facial, bimetallic complexes wherein a bridging ligand binds to both metallic centers, exceptional closeness between the latter as could be suggested by intermetallic distances shorter than the sum of the respective van der Waals radii [1], unavoidably raises the issue of intermetallic bonding [2].

A few years ago, a new class of *syn*-facial heterobimetallic, helical and stable compounds were synthesized by the sequential reaction of organolithium reagents and methyltriflate with cyclomanganated (η^6-arene)$Cr(CO)_3$ complexes [3,4]; the key intermediate being a transient Fischer-type manganese-alkylidene species (Scheme 1).

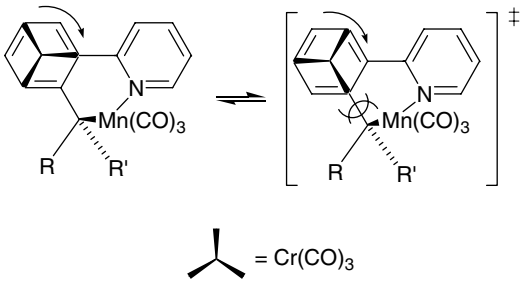
It was established that the *syn*-facial position of the $Mn(CO)_3$ moiety and the $Cr(CO)_3$ rotor in the product

* Corresponding author: Tel.: +33 3 90 24 15 23; fax: +33 3 90 24 50 01.
E-mail addresses: djukic@chimie.u-strasbg.fr (J.-P. Djukic), sercomrx@chimie.u-strasbg.fr (A. de Cian).
[1] To whom requests pertaining to X-ray diffraction analyses should be addressed.

0022-328X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2005.10.029



Scheme 1.

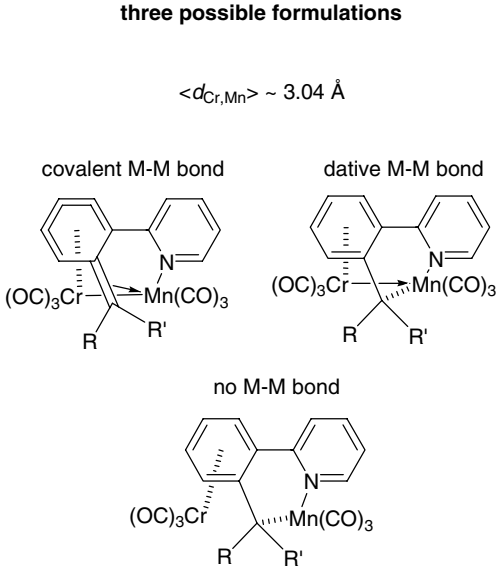


Scheme 2.

stemmed from the manner the alkylidene species was generated and inserted into the C_{Ar}–Mn bond. Similar reactions carried out with chromium-free substrates led to coordinatively saturated Mn(I) species in which two valence-shell electrons formally lost upon insertion of the alkylidene ligands were ''recovered'' by the metal through η^2-bonding with the vicinal phenylene fragment [5]. In the presence of a sterically demanding $Cr(CO)_3$ group, the critical insertion step would lead the Mn(I) to electronic unsaturation unless the chromium bound group takes part in some auxiliary stabilization: this issue deserved a thorough attention given the sparse occurrence of similar cases [6]. *Syn*-facial Cr,Mn benzyl complexes fall into the problematic of the electron-counting in polynuclear species as raised in the past by Hock and Mills [2a] with an historical di-iron organometallic species. In fact, thanks to the seminal work of Pomeroy and co-workers [7], the concept of dative metal → metal bond has widened the scope as electron saturated metals could be assimilated to some extent to ligands.

Syn-facial (Cr,Mn) benzyl complexes display structural similarities with benzyl-bridged Cr,Pd complexes reported by Kalinin and co-workers [8] in the early 90s, which could have given some credit to the hypothesis of a Cr–Mn covalent bond.

In fact, the restricted rotation of the $Cr(CO)_3$ tripod ($\Delta G^{\neq}_{rot} = 15$ kcal mol^{-1} at 253 K) [9], which was evidenced by variable temperature ^{13}C NMR spectroscopy with a ^{13}C-enriched sample (Scheme 2), gives more weight to a hypothetical diffuse and rather weak dative Cr → Mn interaction somewhat akin to that assumed in *syn*-facial indenyl-bridged (Cr,Ir) and (Cr,Rh) complexes [10] and in a few cases of (η^6-aryl)$Cr(CO)_3$-substituted polynuclear ruthenium clusters [11] given that bond formation energies of dative intermetallic interactions are expected to be of a magnitude similar to those of the covalent ones, according to Nakatsuji et al. [12]. To this date, the existence of a Cr–Mn bond remains an unsettled issue. We recently undertook to resolve this question in two steps: (1) by providing evidence that the *syn*-facial arrangement is a general trend of the reaction involving the insertion of an alkylidene into a C_{Ar}–Mn bond (this article), and (2) by investigating theoretically the topological properties [13] of electronic interactions in the *syn*-facial Cr,Mn benzyl complexes.



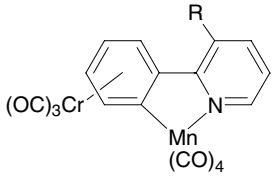
This article presents new examples of *syn*-facial heterobimetallic Cr,Mn benzyl complexes synthesized by a heat-promoted coupling reaction of unsymmetrical diazoalkanes with cyclomanganated 2-[tricarbonyl(η^6-phenyl)chromium]-pyridine. We show that the stereochemical course of the key thermolytic alkylidene insertion step can be controlled by adjusting the steric bulk of substituents of the diazoalkane.

2. Results and discussion

2.1. The limitations of the ''E.O. Fischer-like'' protocol

The stereoselective formation of *syn*-facial Cr,Mn benzyl complexes by the sequential reaction of organolithium reagents and hard electrophiles has one major limitation, which is related to the high reactivity of RLi reagents towards heterocycles. It was previously shown that a strict 1:1 ratio between RLi and the manganese substrate was necessary in order to avoid the double addition of RLi to

the substrate, e.g., at both the $Mn(CO)_4$ fragment and the pyridyl group as exemplified by the reaction that leads to **2a** starting from **1a** (Scheme 3).



1a, R= H
1b, R= Me

In the present work, this drawback was further verified when compound **1a** was treated sequentially first with 1 eq PhLi at −50 °C and a few minutes later with one equivalent of *n*-BuLi at −20 °C. The resulting reaction medium treated with a large excess of MeOTf delivered the brownish compound **2b** in 44% yield after purification, of which the structure was assessed by ^{1}H and ^{13}C NMR spectroscopy (Scheme 3). The *endo* position of the phenyl ring was deduced by ^{1}H NMR and ^{1}H–^{1}H COSY experiments, all five protons of this group resonating at separate chemical shifts, which is clearly symptomatic of a hindered phenyl group in a non-symmetric environment. Unfortunately, **2b** could not be structurally characterized which undermined the assessment of the relative configurations at the dihydropyridyl group.

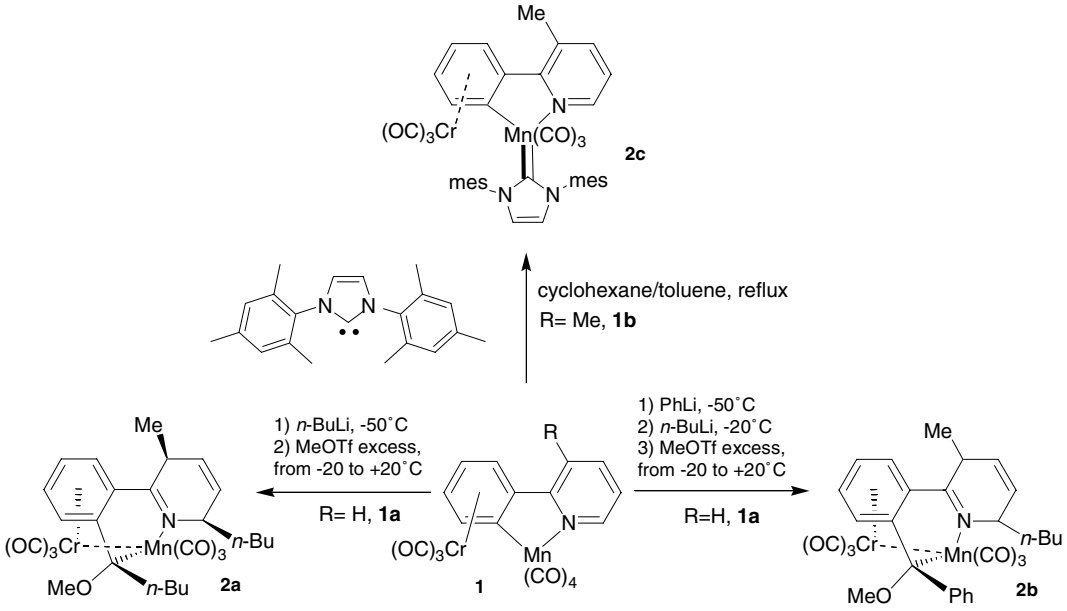
2.2. The thermolytic coupling with alkylidenes and sources of alkylidenes

As an alternative method of preparation of dinuclear *syn*-facial Cr,Mn benzyl complexes, it was previously shown that the thermolytic coupling of the symmetric diphenyldiazomethane is more convenient [14]. This method differs from the "E.O. Fischer-type protocol" by the neutral nature of the intervening reagents and by the relatively high temperatures, which are required in order to promote the creation of a vacant coordination site at the Mn(I) atom to allow the formation of the metal–alkylidene precursor.

2.2.1. The thermo-promoted stereoselective coordination of a relatively stable heterocyclic alkylidene

Although the geometry of the putative coordinatively unsaturated intermediate is not known, it is assumed that the coordination of any incoming σ-donating ligand is thermodynamically controlled to give the more stable *fac*-$LL'L''Mn(CO)_3$ complex in which steric interactions should be minimized [15]. This has been previously already verified in many instances with phosphines as the incoming ligand in the thermolytic conversion of tetracarbonylmanganese chelates into *fac*-tricarbonyl manganese complexes [16].

In this study, this trend could be further verified by reacting complex **1b** at ca. 80–90 °C with a σ-donating alkylidene such as Arduengo's 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene [17], which afforded a stable manganese (I) alkylidene product **2c** in ca. 60% yield (Scheme 3). The latter did not show any ability to further undergo the insertion of the alkylidene fragment into the C_{Ar}–Mn bond. This is not surprising since alkylidenes electronically stabilized by two adjacent heteroelements are known to display weak or no electrophilic behaviour at all [18]. The molecular structure of **2c** could be readily assessed by X-ray diffraction analysis. Table 1 lists the acquisition parameters and refinement data for all the structures reported in this article.



Scheme 3.

Table 1
Listing of X-ray diffraction acquisition parameters and refinement data for complexes **2c**, **3a**, **3c**, **4b**, **5b**, **6b**

Compound	**2c**	**3a**	**3c**	**4b**	**5b**	**6b**
Formula	$C_{39}H_{34}CrMnN_3O_6$	$C_{21}H_{18}CrMnNO_6Si$	$C_{19}H_{10}CrMnNO_7$	$C_{25}H_{16}CrMnNO_6$	$C_{28}H_{22}CrMnNO_6$	$C_{37}H_{28}CrFeMnNO_6$
Molecular weight	747.63	515.40	471.23	533.34	575.42	745.42
Crystal system	Orthorhombic	Orthorhombic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	*Pbca*	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P2_1/n$
a (Å)	11.4850(2)	14.1419(4)	6.1069(1)	8.3957(2)	32.9752(7)	14.1473(3)
b (Å)	16.8920(2)	16.3995(5)	10.8359(2)	9.6675(3)	9.2223(2)	12.6744(2)
c (Å)	18.0700(2)	19.1810(7)	14.4478(3)	14.2536(5)	16.7524(4)	17.9946(4)
α (°)			101.334(5)	77.979(5)		
β (°)			95.776(5)	85.932(5)	106.210(5)	106.343(5)
γ (°)			100.828(5)	70.443(5)		
V (Å^3)	3505.66(8)	4448.5(4)	911.29(3)	1066.25(6)	4892.0(2)	3096.2(1)
Z	4	8	2	2	8	4
Colour	Orange	Red	Orange	Red	Red	Yellow
Crystal dimension (mm)	$0.20 \times 0.10 \times 0.10$	$0.18 \times 0.12 \times 0.07$	$0.20 \times 0.18 \times 0.14$	$0.20 \times 0.12 \times 0.02$	$0.20 \times 0.12 \times 0.08$	$0.08 \times 0.08 \times 0.06$
D_{calc} (g cm^{-3})	1.417	1.54	1.72	1.66	1.56	1.60
$F(000)$	1544	2096	472	540	2352	1520
μ (mm^{-1})	0.722	1.147	1.333	1.146	1.006	1.259
T (K)	173	293	173	173	173	173
Scan mode	'ϕ scans'	'ϕ and ω scans'	'ϕ scans'	'ϕ scans'	'ϕ scans'	'ϕ scans'
hkl Limits	−16/16, −23/23, −25/25	−18,18/−21,21/−24,24	−8,8/−15,15/−19,20	−10,11/−11,13/−19,19	−42,42/−10,11/−21,21	0,19/0,17/−25,24
θ Limits (°)	1.65/30.02	2.5/27.48	2.5/30.05	2.5/29.12	2.5/27.52	2.5/30.01
Number of data measures	10167	10145	7545	8280	9931	9398
Number of data with $I > 3\sigma(I)$	8326[a]	2872	4229	3321	3699	6039
Number of variables	451	280	262	307	334	427
R	0.0433	0.032	0.036	0.035	0.030	0.062
R_w	0.1059	0.039	0.057	0.039	0.037	0.072
Goodness-of-fit	1.071	1.059	1.083	1.042	1.072	1.016
Largest peak in final difference (e Å^{-3})	0.540	0.293	0.591	0.333	0.133	0.855

[a] Number of data with $I > 2\sigma(I)$.

The ORTEP diagram in Fig. 1 shows the *anti* relationship existing between the heterocyclic alkylidene ligand and the $Cr(CO)_3$ rotor [19]. The planar mesityl groups are almost perfectly perpendicular to alkylidene's heterocycle. Like other octahedral carbonylmetalalkylidene complexes [20], the hindrance introduced by this bulky alkylidene causes a slight distortion of the coordination environment around the Mn(I) centre illustrated by a slight bending of the Mn–C(38)–O(6) angle, which amounts 169.7(2)°. The shortest distance separating the pyridyl ring from the proximal mesityl group, e.g., C(13)–N(3), amounts 3.112(3) Å. The alkylidene's heterocycle faces the chromium-bound aryl fragment with a torsion angle C(22)–Mn–C(12)–N(1) amounting 63.9(2)°. Although ^{1}H NMR spectroscopy (300 MHz) did not reveal any peculiar dynamic behaviour, which could be expected for such hindered complexes, the rotation of the alkylidene fragment around the Mn–C(12) axis is not restrained. At room temperature, the diastereotopic mesityl's methyl groups were detected as three separated narrow singlets at 2.27, 2.03 and 1.79 ppm. ^{13}C NMR spectroscopy revealed the typical "shielded" alkylidene's signal at 193.1 ppm in $CDCl_3$. The IR spectrum of **2c** in the carbonyl-ligand stretching region displayed five bands resulting from the superimposition of the three bands generated by the asymmetric *fac*-$Mn(CO)_3$ moiety at 2000, 1943 and 1885 cm^{-1} and the two bands generated by the fast-rotating pseudo-symmetric *fac*-$Cr(CO)_3$ moiety at 1913 and 1866 cm^{-1}.

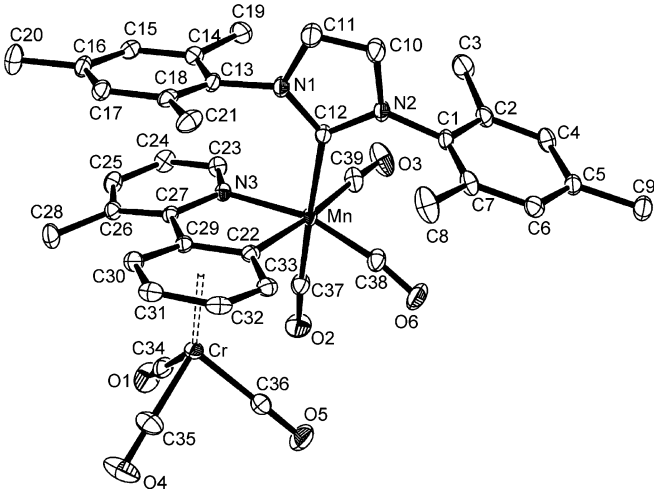
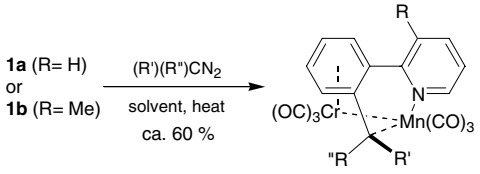


Fig. 1. ORTEP diagram of the structure of compound **2c**. Ellipsoids are drawn at 30% probability level. Atoms of hydrogen have been omitted for clarity. Selected interatomic distances (Å): Mn–C(12), 2.121(2); Mn–C(22), 2.028(2); Cr–C(22), 2.317(2); Mn–N(3), 2.0877(18); C(10)–C(11), 1.336(5); N(1)–C(12), 1.363(3); N(2)–C(12), 1.378(3); N(2)–C(10), 1.382(4); N(1)–C(11), 1.379(4); O(3)–C(39), 1.150(4); O(2)–C(37), 1.152(4); O(6)–C(38), 1.164(4); C(1)–C(38), 3.031(3); C(13)–N(3), 3.112(3). Selected interatomic angles and torsions (°): Mn–C(38)–O(6), 169.7(2); C(29)–C(22)–C(33), 115.9(2); N(3)–Mn–C(12)–N(1), 14.7(2); C(22)–C(29)–C(27)–N(3), 10.7(3); C(38)–Mn–C(12)–N(2), 27.2(2). Selected interplanar angles (°) with planes P_1(C(13),C(14),C(15),C(16),C(17),C(18)),P_2(N(3),C(23),C(24),C(25),C(26),C(27)),P_3(N(1),C(12),N(2),C(10),C(11)),P_4(C(1),C(2),C(4),C(5),C(6),C(7)): P_1–P_2, 10.7; P_1–P_3, 86.6; P_3–P_4, 84.4.

2.2.2. Coupling reactions with substituted diazomethanes

We undertook a systematic study of the reactivity of substrates **1a** and **1b** with four diazoalkanes: $(Me_3Si)(H)CN_2$, $(Ph)(Me)CN_2$ [21], $(Ph)(t\text{-}Bu)CN_2$ [22] and $(Ph)(CH_2CH_2Fc)CN_2$ in order to evaluate the factors relevant to the stereoselectivity of such heat-promoted coupling (Eq. (1)) (Table 2). We expected indeed the formation of *syn*-facial Cr,Mn benzyl complexes to be much less stereoselective by this thermolytic method, the alkylidene-insertion key step taking place at a temperature up to 120 °C higher than in the conditions reported for the so-called "E.O. Fischer-type" procedure.



R= H: **3a**, R"= $SiMe_3$, R'= H; **3b**, R"= H, R'= $SiMe_3$; **4a**, R"= Ph, R'= Me; **4b**, R"= Me, R'= Ph; **5a**, R"= Ph, R'= *t*-Bu; **5b**, R"= *t*-Bu, R'= Ph

R= Me: **6a**, R"= Ph, R'=CH_2CH_2Fc; **6b**, R"=CH_2CH_2Fc, R'=Ph

(1)

The importance of steric hindrance over stereoselectivity was addressed by treating **1a** with an excess of $(Me_3Si)(H)CN_2$ in a boiling 10:1 mixture of *n*-heptane and toluene. The reaction afforded as expected a mixture of the two isomers **3a** and **3b**, respectively, in a 6.7:1 ratio, the latter containing the Me_3Si group *endo* with respect to the pyridyl group. The rate of formation of *syn*-facial Cr,Mn benzyl complexes **3a** and **3b** was estimated qualitatively by running a series of reactions between 2.5 equivalents of $(Me_3Si)(H)CN_2$ and **1a** in a boiling mixture of 15 mL of cyclohexane and 1 mL of toluene. These experiments showed that the reaction reached completion 15 min after the end of the addition of $(Me_3Si)(H)CN_2$. At all stages of the reaction, **3a** largely predominated. The rough 3:1 ratio between isomers **3a** and **3b** remained roughly constant over long periods of time.

The preponderance of isomer **3a** over **3b** is seemingly the consequence of a pure steric control, which privileged the formation of the less encumbered product. This rule was apparently contradicted by the result of the reaction of an excess of $(Ph)(Me)CN_2$ with **1a**, which afforded an

Table 2
Conversions and product ratios for the reactions of **1a** and **1b** with $(Ph)(R)CN_2$ (R = Me,*t*-Bu, CH_2CH_2Fc)

Diazoalkane	Solvents (ratio)	Conversion (%)	Products (ratio)
$(Ph)(Me)CN_2$	*n*-hexane/ toluene (10:1)	60	**4a**:**4b** (1:3)
$(Ph)(t\text{-}Bu)CN_2$	*n*-hexane/ toluene (10:1)	59	**5a**:**5b** (0:1)
$(Ph)(FcCH_2CH_2)CN_2$	*n*-heptane/ toluene (10:1)	79	**6a**:**6b** (1:6.7)

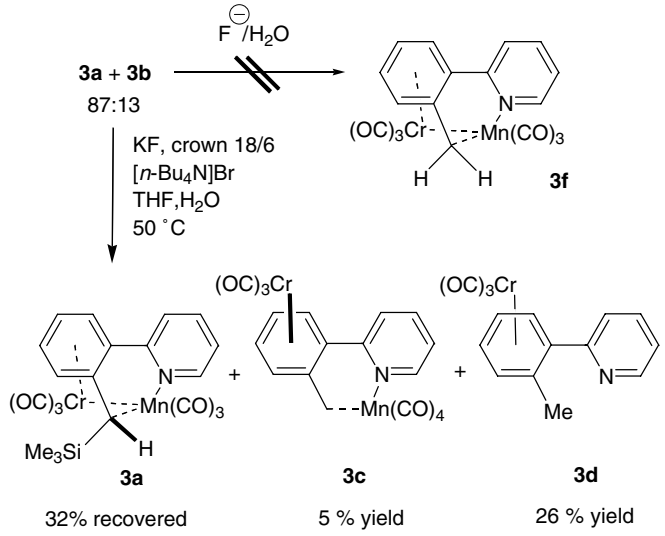
air sensitive mixture of two isomers **4a** and **4b** in a 1:3 ratio; the major component **4b** bearing the phenyl ring in an *endo* fashion, above the pyridyl ligand. The preference given to isomer **4b** is reminiscent of the stereoselectivity observed with reactions carried out at a much lower temperature under the so-called E.O. Fischer-type conditions to afford *exo*-alkoxy, *endo*-phenyl-substituted *syn*-facial Cr,Mn benzyl complexes. This further underlines the active role of the phenyl group in the stereoselective *cis*-migration step, already highlighted in a previous article [4].

These results indicate that reasonable stereoselectivity for the coupling of alkylaryldiazomethanes can be reached even at high temperatures by adjusting the steric volume of the alkyl group. This was verified by undertaking the reaction of (Ph)(*t*-Bu)CN_2 with **1a**, which resulted in the formation of a sole product **5b**, bearing the *t*-Bu group at the *exo* position, in 59% yield. The reaction of (Ph)($FcCH_2CH_2$)-CN_2 with **1b** afforded a mixture of complexes **6a** and **6b** in a 6.7:1 ratio. If compared to the results obtained for **4a** and **4b**, the latter indicate that a slight steric demand combined to the abovementioned "phenyl group effect" increases the stereoselectivity of the coupling reaction.

2.3. The structural characterization of *3a, 4b, 5b* and *6b* by X-ray diffraction analyses

In our hands, the separation and isolation of pure stereoisomers resulting from reactions with (Ph)(Me)CN_2, (Me_3Si)(H)CN_2 and with (Ph)($FcCH_2CH_2$)CN_2, e.g., **3a**–**b** and **4a**–**b** and **6a**–**b** by conventional chromatographic methods failed in many cases. Recovery of pure samples could be achieved only either by repeated recrystallisation or chemical treatment.

A pure sample of **3a** was obtained by submitting a mixture of **3a** and **3b** to desilylation conditions, which consisted of a treatment with an aqueous solution of a fluoride (Scheme 4).



Scheme 4.

Even though both isomers underwent desilylation, isomer **3b** was completely consumed and the overall result of this reaction was a new mixture containing remnants of **3a**, a new dinuclear complexes **3c**, **3d** and 2-(*o*-tolyl)pyridine (Scheme 4).

The structures of the two latter products were fully assessed by comparing their spectroscopic and analytical data to those of an original sample prepared by the sequential transmetallation and methylation with MeI of complex **3e** (Eq. (2)) [23]. The origin of complex **3c** is not clear yet although it might be, like **3d**, the decomposition of the expected desilylation product **3f**, which could not be isolated nor observed. Compound **3c** was successfully crystallized and its structure resolved by X-ray diffraction analysis. The ORTEP diagram displayed in Fig. 2 indicates that the two metal-centred moieties are *anti*-facial and that the Mn atom is part of a folded six-membered metallacycle. Upon chromatographic treatment, a clean sample of **3a**

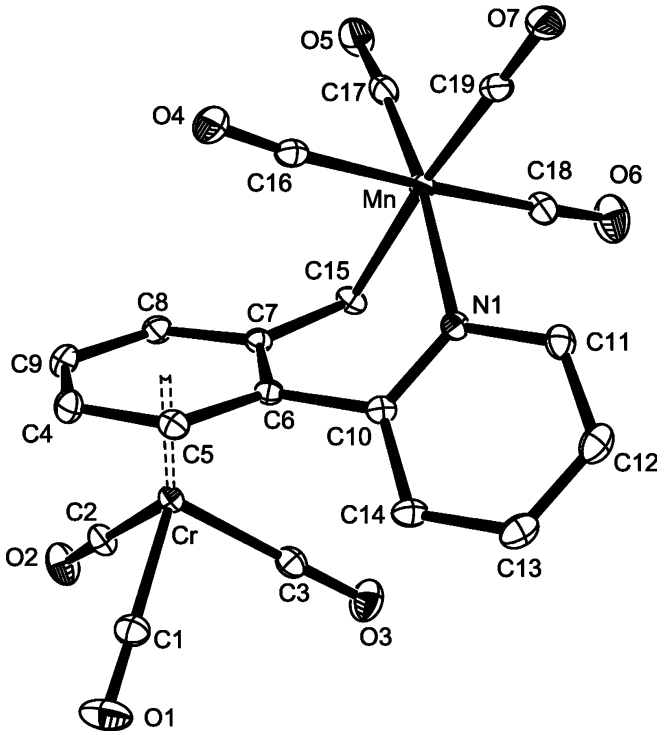
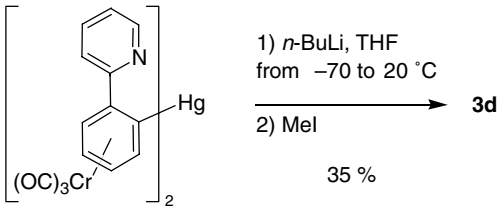


Fig. 2. ORTEP diagram of the structure of compound **3c**. Ellipsoids are drawn at 30% probability level. Atoms of hydrogen have been omitted for clarity. Selected interatomic distances (Å): Mn–C(15), 2.148(2); Mn–C(6), 3.253(3); Mn–C(7), 2.897(3); C(7)–C(15), 1.475(3); C(6)–C(10), 1.487(3); C(13)–C(14),1.376(3); Mn–N, 2.100(2); Mn–C(16), 1.870(2); Mn–C(17), 1.800(2); Mn–C(18), 1.859(2); Mn–C(19), 1.844(2); Mn–Cr, 5.080(3); Cr–C(4), 2.215(2); Cr–C(5), 2.187(2); Cr–C(6), 2.209(2); Cr–C_{ipso}(7), 2.291(2); Cr–C(8), 2.238(2); Cr–C(9), 2.212(2). Selected interatomic angles and torsions (°): C(1)–Cr–C(2), 87.44(9); C(2)–Cr–C(3), 90.76(9); C(1)–Cr–C(3), 87.8(1); Mn–C(15)–C(7), 104.7(9); C(15)–Mn–C(18), 85.78(8); C(16)–Mn–N, 93.45(7); N–C(10)–C(6)–C(7), 43.6; C(14)–C(10)–C(6)–C(5), 45.5.

was recovered, successfully crystallized and analyzed by X-ray diffraction (Fig. 3).



3e

Complex **4b** was crystallized by the diffusion technique applied to a solution of a mixture of **4b** and **4a**. Complex **5b** crystallized at −18 °C from CH_2Cl_2 upon diffusion into *n*-heptane in a narrow sample tube. Repeated chromatographic treatment of mixtures of **6a**–**b** only allowed the isolation of limited amounts of pure **6b**, which was crystallized and subsequently submitted to X-ray diffraction analysis. Figs. 3–6 display the ORTEP diagrams of **3a**, **4b** (Fig. 4), **5b** (Fig. 5), **6b** (Fig. 6) drawn at the 30% probability level.

The Mn-to-Cr distance in all cases amounts ca. 3.04 Å, an average value observed previously in analogous complexes bearing alkoxy groups at the benzylic position. The largest intermetallic distance is noticed for **3a** (Fig. 3). In all four cases, the arene ring bound

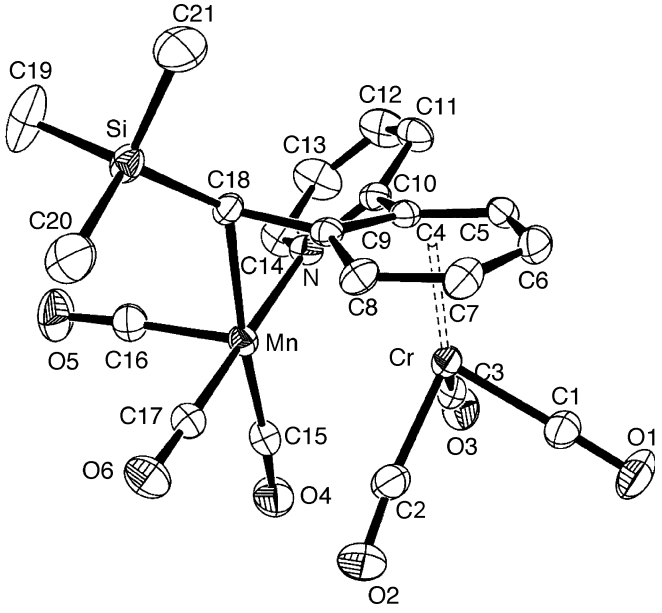


Fig. 3. ORTEP diagram of the structure of compound **3a**. Ellipsoids are drawn at 30% probability level. Atoms of hydrogen have been omitted for clarity. Selected interatomic distances (Å): Cr–Mn, 3.076(6); C(18)-Si, 1.878(3); Mn–C(18), 2.154(3); Mn–C(14), 2.399(6); Mn–C(4), 2.947(6); Mn-(N), 2.101(3); Mn–C(15), 1.815(4); Mn–C(16), 1.776(4); Mn–C(17), 1.807(4); Cr–C(4), 2.225(3); Cr–C(5), 2.226(4); Cr–C(6), 2.208(4); Cr–C(7), 2.231(4); Cr–C(8), 2.267(3); Cr–C(9), 2.434(6); C(18)–C(9), 1.435(5). Selected interatomic angles and torsions (°): C(14)–C(18)–Mn, 81.2(5); C(15)–Mn–C(16), 94.3(8); C(2)–Cr–C(1), 83.8(1); C(2)–Cr–C(3), 93.9(0); C(1)–Cr–C(3), 84.3(8); N–C(10)–C(4)–C(9), 40.3(3); C(7)–C(6)–C(5)–C(4), 10.2(8); C(7)–C(8)–C(9)–C(4), 6.6(5); C(8)–C(9)–C(4)–C(5), 14.6(6); C(18)–C(14)–C(4)–C(10), 15.0(8).

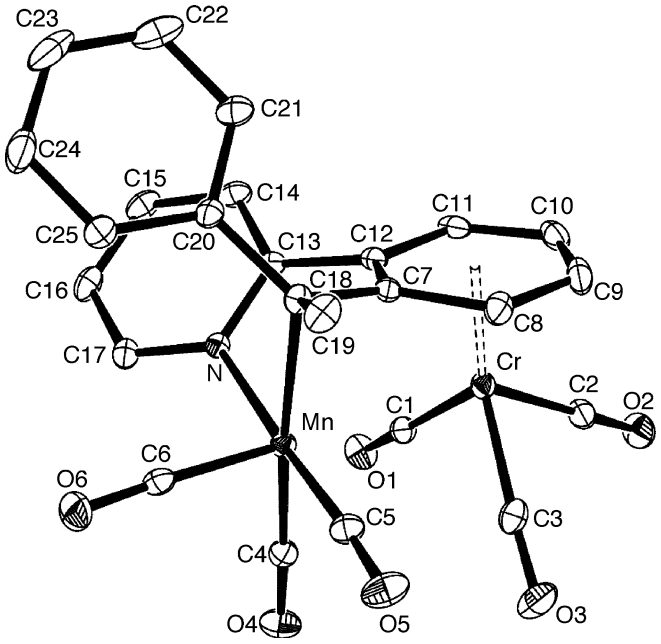


Fig. 4. ORTEP diagram of the structure of compound **4b**. Ellipsoids are drawn at 30% probability level. Atoms of hydrogen have been omitted for clarity. Selected interatomic distances (Å): Cr–Mn, 3.047(6); Mn–C(18), 2.175(3); Mn–N, 2.063(2); Cr–C(7), 2.419(3); Cr–C(12), 2.218(3). Selected interatomic angles and torsions (°): C(3)–Cr–C(1), 95.0(1); C(2)–Cr–C(3), 83.7(1); N–C(13)–C(12)–C(7), 39.7; C(9)–C(8)–C(7)–C(6), 6.4; C(6)–C(5)–C(4)–C(9), 9.6. Centroid to centroid distance between pyridyl and phenyl rings: 3.641(6) Å.

to Cr is slightly folded seemingly as a consequence of the entanglement caused by the static $Mn(CO)_3$ fragment. This folding can be evaluated by the measure of dihedral angles defined by the carbon atoms located between *ipso* and *para* positions at the arene. In **5b**, such dihedral angles amount the highest values of 12.7° and 9.2°. Another parameter that indicates the degree of geometrical distortion of the (phenylene)tricarbonylchromium fragment is the Cr–C_{ipso} distance, which is, in all cases, higher than the average Cr–C_{Ar} bond distance of ca. 2.20 Å. Even though crystal packing forces may drastically influence local geometries, the distortions that can be noticed in these new (η^6-arene)tricarbonylchromium complexes may result from interplay between steric and purely electronic effects of the substituents [24] at the benzylic position. For instance, bulky alkyl groups such as *t*-Bu in **5b** may enter in sensible steric interaction with the adjacent Cr-bonded-phenylene ligand, which should induce a slight rotation around the C_{ipso}–C_{benzyl} bond thus reducing the distance between the *endo*-phenyl and pyridyl groups. The observed slight decrease of the centroid-to-centroid Ph-to-py distances from **4b** and **6b** (3.641(6) and 3.690(6) Å, respectively) to **5b** (3.502(5) Å) would be consistent with an increase of steric interaction between the alkyl substituent at the benzylic position and the Cr-bound phenylene ligand following the order $FcCH_2CH_2$- ~ Me- < *t*-Bu-.

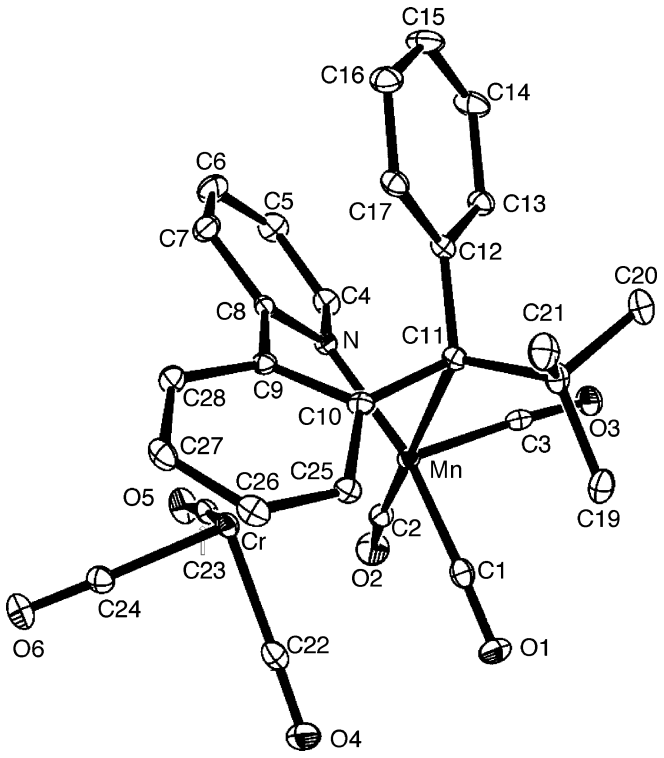


Fig. 5. ORTEP diagram of the structure of compound **5b**. Ellipsoids are drawn at 30% probability level. Atoms of hydrogen have been omitted for clarity. Selected interatomic distances (Å): Mn–Cr, 3.040(4); Mn–C(10), 2.345(4); Mn–C(11), 2.280(4); Mn–N, 2.062(2); Cr–C(10), 2.479(3); Cr–C(9), 2.218(2). Selected interatomic angles and torsions (°): C(23)–Cr–C(22), 95.5(1); C(3)–Mn–C(11), 83.23(9); C(27)–C(26)–C(25)–C(10), 9.2; N–C(8)–C(9)–C(10), 38.5; C(27)–C(28)–C(9)–C(10), 12.7. Centroid to centroid distance between pyridyl and phenyl rings: 3.502(5) Å.

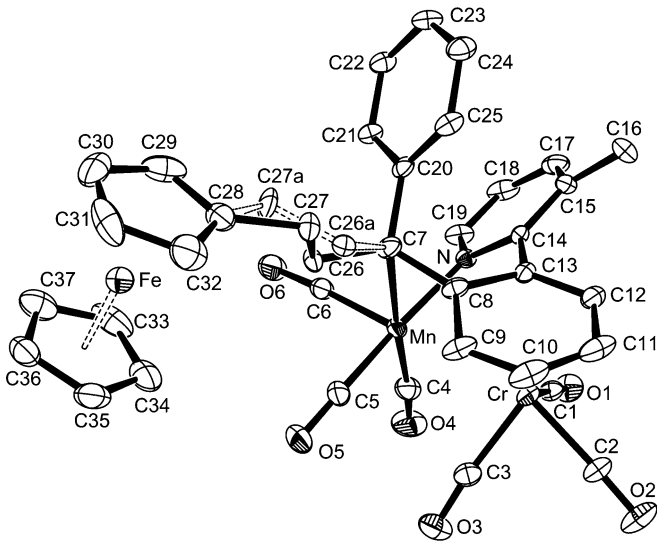


Fig. 6. ORTEP diagram of the structure of compound **6b**. Ellipsoids are drawn at 30% probability level. Atoms of hydrogen have been omitted for clarity. Atoms C(26) and C(27) which are subjected to positional disorder have been drawn at the sites they occupy with 50% probability of occupancy. Selected interatomic distances (Å): Cr–Mn, 3.011(9); Mn–C(8), 2.343(4); Mn–C(7), 2.203(3); Mn–N, 2.044(3); Cr–C_{ipso}(8), 2.449(5); Cr–C(9), 2.241(5). Selected interatomic angles and torsions (°): C(1)–Cr–C(2), 85.7(2); C(3)–Cr–C(1), 92.8(2); C(6)–Mn–C(7), 88.2(2); C(8)–C(9)–C(10)–C(11), 10.1; C(8)–C(13)–C(12)–C(11), 8.1; N–C(14)–C(13)–C(8), 40.6. Centroid to centroid distance between pyridyl and phenyl rings: 3.690(6) Å.

3. Conclusion

In this article, we have shown that the coupling of unsymmetrical diazomethanes with derivatives of cyclomanganated 2-[tricarbonyl(η^6-phenyl)chromium]pyridine is efficient, leading to new examples of chemically stable *syn*-facial Cr,Mn benzyl complexes, among which four have been structurally characterized and possess structural features similar to those noticed with complexes prepared by a different method. We have shown that the stereochemical course of the coupling reaction can be influenced by bulky alkyl substituents even at temperatures well above +20 °C. The nature of the electronic interactions between the two metal centres in *syn*-facial Cr,Mn benzyl complexes is currently being addressed by quantum mechanical methods; the results of this study shall be disclosed in due time.

4. Experimental

4.1. General

All experiments were carried out under a dry atmosphere of argon with distilled, dried and degassed solvents. Complexes **1a** [25] and **1b** [3] were synthesized according to published procedures. Diazoalkanes (Ph)(Me)CN_2 and (Ph)(*t*-Bu)CN_2 were prepared by oxidation of the corresponding hydrazones with yellow HgO at room temperature. Trimethylsilyldiazomethane in solution in *n*-hexane was purchased from Aldrich Chem. Co. and used without further purification. NMR spectra were acquired on Bruker *Avance* 500 (^{13}C and ^{1}H nuclei) and AC 300 (^{1}H nucleus) spectrometers at room temperature unless otherwise stated. Chemical shifts are reported in parts per million downfield of Me_4Si. IR spectra were measured with a Perkin–Elmer FT spectrometer. Mass spectra (FAB+) were recorded at the Service of Mass Spectrometry of University Louis Pasteur and at the Analytical Centre of the Chemical Institute of the University of Bonn (EI). Elemental analyses (reported in % mass) were performed at the Service d'Analyses of the "Institut de Chimie de Strasbourg" and at the analytical centre of the "Institut Charles Sadron" in Strasbourg.

4.2. Procedure for X-ray diffraction analysis and structure resolution for **2c**, **3a**, **3c**, **4b** and **5b** and **6b**

Acquisition and processing parameters are displayed in Table 1. Reflections were collected with a Nonius KappaCCD diffractometer using Mo Kα graphite monochromated radiation ($\lambda = 0.71073$ Å). The structures of **3a**, **3c**, **4b**, **5b** and **6b** were solved using direct methods, they were refined against $|F|$ and for all pertaining computations, the Nonius OpenMoleN package was used [26]. For complex **2c**, the structure was solved using SHELXL-97 [27]. Hydrogen

atoms were introduced as fixed contributors. The absolute structure of **2c** ($x = -0.021(14)$) was determined by refining the corresponding Flack's x parameters.

4.3. 3-Ferrocenyl, 1-phenyl, 1-diazopropane, (Ph)($FcCH_2CH_2$)CN_2

1-Phenyl-3-ferrocenyl-2-propanone (0.4 g, 1.26 mmol) obtained from 1-phenyl-3-ferrocenyl-2-propenone following published procedures [28], was converted into its hydrazone derivative by reaction with hydrazine monohydrate (3 mL, 62 mmol) in absolute ethanol (3 mL) after 12 h of reflux. The resulting solution was concentrated to a third of its original volume and let to boil for additional 3 h. A volume of absolute ethanol (3 mL) was added and the reaction was finally halted after the mixture has had boiled for additional 3 h. The mixture was then extracted with Et_2O and the organic phase washed thrice with water, once with brine and dried over Na_2SO_4. Removal of solvents under reduced pressure afforded an oily mixture of the Z and E isomers (82:18) of 1-phenyl-3-ferrocenyl-2-propanone hydrazone (0.37 g, 89% yield) of reasonable purity but quite unstable in character. The latter (0.32 g, 0.96 mmol) was then dissolved in dry distilled $CHCl_3$ (35 mL) and the solution added with freshly prepared activated MnO_2 (0.8 g, 9.2 mmol). The suspension was let to react 10 min at room temperature and was rapidly filtered through a short column containing two superimposed pads of glucose and Na_2SO_4. The deep red coloured filtrate was then swiftly stripped of solvent and the residue used without purification in further reactions that had to be carried out immediately upon isolation of this reagent. This diazoalkane could not be satisfactorily characterized analytically due to its high chemical instability. IR spectroscopy, however, confirmed the quantitative conversion of the hydrazone. (Ph)($FcCH_2CH_2$)C=N–NH_2: HRMS (FAB+) calcd for $C_{19}H_{20}N_2{}^{56}Fe$: 332.097576. Found: 332.097588. Major isomer: ^{1}H NMR ($CDCl_3$) δ 7.66 (d, $^3J = 7.1$ Hz, 2H), 7.35 (m, 3H), 5.20 (m, 2H), 4.11 (s, 9H), 2.83 (t, $^3J = 7.6$ Hz, 2H), 2.61 (t, $^3J = 7.6$ Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 150.5$, 138.5, 128.5 (2C), 128.2, 125.7 (2C), 87.9 (1C, Cp), 68.7 (5C, Cp), 68.2 (2C, Cp), 67.9 (2C, Cp), 27.7, 25.9 ppm. Minor isomer: ^{1}H NMR ($CDCl_3$) δ 7.48 (m, 2H), 7.32 (m, 3H), 5.09 (m, 2H), 4.09 (s, 9H), 2.70 (m, 2H), 2.54 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$) δ 151.8, 134.6, 129.3 (2C), 128.8, 127.5 (2C), 88.6 (1C, Cp), 68.6 (5C, Cp), 68.0 (2C, Cp), 67.2 (2C, Cp), 39.5, 26.8 ppm. (Ph)($FcCH_2CH_2$)CN_2: IR (CH_2Cl_2) ν (N_2) 2039 (s) cm^{-1}.

4.4. Tricarbonyl[2-{tricarbonyl{1′,2′,3′,4′,5′,6′-η-2′-[(exo-methoxy)(phenyl)methylene-κ$C^{7'}$]phenyl}chromium}(6-n-butyl,3-methyl,3,6-dihydropyridine-κN)]manganese (Cr,Mn) (**2b**)

A solution of complex **1a** (400 mg, 0.87 mmol) in 1,2-dimethoxyethane (20 mL) was cooled to −60 °C and treated with one equivalent of PhLi (0.5 mL, 1.8 M, 0.90 mmol). The reaction medium was stirred for 10 min at −60 °C, warmed to −40°C and one equivalent of n-BuLi (0.55 mL, 1.6 M, 0.88 mmol) was added. The resulting mixture was slowly warmed to −20 °C over 30 min and treated with an excess amount of neat methyltriflate (0.75 mL, 6.63 mmol). The resulting dark brown solution was allowed to warm to room temperature and was stripped of solvent under reduced pressure. The raw residue was dissolved in CH_2Cl_2, silica gel was added, and the solvent evaporated under reduced pressure. The coated silica gel was loaded on the top of a jacketed column of SiO_2 packed in dry n-hexane and cooled at +5 °C. A brown band containing complex **2b** was eluted with a 9:1 mixture of CH_2Cl_2 and n-hexane. Compound **2b** was recovered as a brown powder that was further purified by recrystallisation in n-hexane to yield brown needles (240 mg, 44% yield). Elem. Anal. Calc. for $C_{30}H_{28}NO_7CrMn$: C, 57.98; H, 4.54; N, 2.25. Found: C, 57.90; H, 4.46; N, 2.24%. HRMS calcd for $C_{30}H_{28}NO_7CrMn$ (FAB+): m/e 621.065134. Found: 621.065553. IR (CH_2Cl_2) ν(CO) 2011 (s), 1961 (s), 1929 (m), 1891 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 8.79 (d, $^3J = 8.0$ Hz, 1H, $H_{Ph\text{-}endo\text{-}ortho}$), 7.54 (t, $^3J = 7.5$ Hz, 1H, $H_{Ph\text{-}endo\text{-}meta}$), 7.18 (t, $^3J = 7.2$ Hz 1H, $H_{Ph\text{-}para}$), 7.13 (d, $^3J = 7.0$ Hz, 1H, $H_{Ph\text{-}exo\text{-}ortho}$), 7.02 (t*, $^3J = 7.3$ Hz, 1H, $H_{Ph\text{-}exo\text{-}meta}$), 6.28 (t*, $^3J = 7.0$ Hz, 1H, $H_{ArCr\text{-}meta}$), 5.44 (dd, $^3J = 4.1$ Hz; $^3J = 9.9$ Hz, 1H, $H_{hydropyr}$), 5.23 (dd, $^3J = 4.4$ Hz; $^3J = 9.9$ Hz, 1H, $H_{hydropy}$), 5.09 (t, $^3J = 7.4$ Hz, 1H, $H_{ArCr\text{-}meta}$), 4.30 (d, $^3J = 6.5$ Hz, 1H, $H_{ArCr\text{-}ortho}$), 4.09 (d, $^3J = 7.5$ Hz, 1H, H_{ArCr}), 3.25 (m, 1H, $H_{6\text{-}hydropyr}$), 3.12 (s, 3H, –OCH_3), 2.27 (m, 1H, $H_{3\text{-}hydropyr}$), 1.29 (m, 1H, $H_{1\text{-}Bu\text{-}exo}$), 1.15–0.85 (m, 4H, $H_{2,3\text{-}Bu}$), 0.89 (d, $^3J = 7.3$ Hz, 3H, –CH_3), 0.78 (t, $^3J = 7.2$ Hz, 3H, –$CH_{3\text{-}Bu}$), −0.64 (m, 1H, $H_{1\text{-}Bu\text{-}endo}$) ppm. ^{13}C NMR ($CDCl_3$) δ 234.8 (CrCO, broad), 230.2 (MnCO), 229.4 (MnCO), 219.7 (MnCO), 176.0, 141.6, 133.9, 129.3, 127.4, 126.7, 126.5, 124.5, 122.8, 91.0, 90.0, 88.7, 84.3, 83.0, 79.2, 79.1, 66.6, 55.1, 35.1, 30.7, 27.9, 22.6, 18.9, 13.9 ppm. MS (FAB+): m/e 621 $[M]^+$, 590 $[M-OCH_3]^+$, 562 $[M-OCH_3-CO]^+$, 537 $[M-3CO]^+$, 453 $[M-6CO]^+$, 398 $[M-6CO-Mn]^+$, 346 $[M-6CO-Mn-Cr]^+$.

4.5. [OC-6-42]-Tricarbonyl{2-[tricarbonyl(1′,2′,3′,4′,5′,6′-η-phenylene-κ$C^{1'}$)chromium]pyridine-κN}[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]manganese (I) (**2c**)

Complex **1b** (492 mg, 1.04 mmol) was dissolved in cyclohexane (10 mL) and the resulting suspension was brought to reflux. A solution of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (479 mg, 1.56 mmol) in toluene (5 mL) was added dropwise in about 15 min and the resulting medium was left to react for additional 40 min. The suspension was stripped from solvents under reduced pressure. The residue was dissolved in CH_2Cl_2 and silica was added to the resulting solution; the suspension was evaporated to dryness and the coated silica loaded on the top of a SiO_2 column packed in n-pentane. Complex **2c** was separated from minor by-products and eluted as a bright orange

band with a mixture of CH_2Cl_2 and *n*-pentane 1:1 at ca. 15 °C. The orange solution containing **2c** was evaporated under reduced pressure and the bright orange crystalline compound was recrystallised from CH_2Cl_2 and *n*-heptane (540 mg, 69% yield). Elem. Anal. Calc. for $C_{39}H_{34}N_3O_6CrMn$: C, 62.65; H, 4.58; N, 5.62. Found: C, 62.55; H, 4.66; N, 5.43%. IR (CH_2Cl_2) *ν*(CO) 2000 (vs), 1943 (vs), 1913 (vs), 1885 (vs), 1866 (vs), 1265 (m), 895(m), 734 (s) cm^{-1}. ^1H NMR ($CDCl_3$) *δ* 8.45 (d, $^3J = 5.5$ Hz, 1H, H_{py}), 7.27 (d, $^3J = 8.3$ Hz, 1H, H_{py}), 6.76–6.73 (m, 6H, $H_{mes} + H_{pyr}$), 6.62 (dd, $^3J = 7.4$ Hz; $^3J = 5.5$ Hz, 1H, H_{py}), 6.16 (d, $^3J = 6.2$ Hz, 1H, $H_{ortho\text{-}ArCr}$), 5.82 (d, $^3J = 6.7$ Hz, 1H, $H_{ortho\text{-}ArCr}$), 5.42 (t*, $^3J = 5.9$ Hz, 1H, $H_{meta\text{-}ArCr}$), 5.12 (t*, $^3J = 6.1$ Hz, 1H, $H_{meta\text{-}ArCr}$), 2.59 (s, 3H, $H_{Me\text{-}py}$), 2.27 (s, 6H, H_{mes}), 2.03 (s, 6H, H_{mes}), 1.79 (s, 6H, H_{mes}) ppm. ^{13}C NMR ($CDCl_3$) *δ* 236.1 (CrCO), 223.6 (MnCO), 217.9 (MnCO), 216.6 (MnCO), 193.1 ($MnC_{alkylidene}$), 162.0, 157.7, 151.1, 139.8, 138.9, 136.7, 135.8, 135.4, 131.8, 129.0, 128.8, 124.8, 122.0, 117.5, 108.3 (C_{ArCr}), 93.7 (C_{ArCr}), 92.8 (C_{ArCr}), 89.7 (C_{ArCr}), 22.9 ($C_{Me\text{-}py}$), 21.0 ($C_{Me\text{-}mes}$), 18.7 ($C_{Me\text{-}mes}$), 18.4 ($C_{Me\text{-}mes}$) ppm.

*4.6. General procedure for the coupling of diazoalkanes with **1a** or **1b***

To a boiling solution of **1a** (or **1b**) a solution of the diazoalkane in an appropriate aliphatic or aromatic solvent was added dropwise over ca. 15 min. Generally, the colour of the solution changed from orange to dark red. The completion of the reaction was verified by IR spectroscopy and the solvent(s) removed under reduced pressure to yield a raw solid mixture that was dissolved in CH_2Cl_2. Silica gel was added to this solution and the solvents were removed under reduced pressure. The coated SiO_2 was loaded on the top of a refrigerated column of silica gel packed in dry *n*-hexane. Fractions containing the main products of the reaction were collected generally by elution with 9:1 mixtures of CH_2Cl_2 and *n*-hexane. In some cases silica gel could be deactivated by hydration with 5% water in acetone in order to minimize the decomposition of sensitive organometallic compounds during chromatographic treatment.

*4.7. fac-Tricarbonyl[2-[tricarbonyl[1′,2′,3′,4′,5′,6′-η-2′-(trimethylsilylmethylene-κC$^{7'}$)phenyl]chromium]pyridine-κN]manganese (Cr,Mn) (**3a** and **3b**)*

Complex **1a** (800 mg, 1.75 mmol), $N_2C(H)(SiMe_3)$ in *n*-hexane (2.2 mL, 2.0 M, 4.40 mmol), *n*-heptane (20 mL), toluene (2 mL), reflux for 20 min. Chromatography on SiO_2, elution with a 3:2 mixture of CH_2Cl_2 and *n*-hexane, complexes **3a** and **3b** were recovered as a red solid mixture (511 mg, 57% yield). Elem. Anal. Calc. for $C_{21}H_{18}O_6NSiCrMn$: C, 48.94; H, 3.52; N, 2.72. Found: C, 48.73; H, 3.52; N, 2.52%. Complex **3a**: Elem. Anal. Calc. for $C_{21}H_{18}O_6NSiCrMn$: C, 48.94; H, 3.52; N, 2.72. Found: C, 48.43; H, 3.49; N, 2.69%. IR (CH_2Cl_2) *ν*(CO) 2008 (s), 1958 (s), 1922 (m), 1896 (m) cm^{-1}. ^1H NMR (CD_2Cl_2) *δ* 7.94 (d, $^3J = 4.9$ Hz, 1H, H_{py}), 7.41 (t*, $^3J = 7.7$ Hz, 1H, H_{py}), 6.85 (m, 2H, H_{py}), 6.22 (t, $^3J = 6.0$ Hz, 1H, H_{ArCr}), 4.85 (t, $^3J = 6.2$ Hz, 1H, H_{ArCr}), 4.35 (d, $^3J = 5.9$ Hz, 1H, H_{ArCr}), 3.51 (d, $^3J = 7.5$ Hz, 1H, H_{ArCr}), 1.15 (s, 1H, C*H*-$SiMe_3$), 0.26 (s, 9H, –$Si(CH_3)_3$) ppm. ^{13}C NMR (CD_2Cl_2, 0 °C) *δ* 235.6 (CrCO), 231.8 (MnCO), 230.4 (MnCO), 222.0 (MnCO), 158.1, 152.7, 138.5, 123.4, 119.7, 99.1, 92.7, 90.9, 89.9, 86.5, 85.0, 21.1, 1.6 ppm. Complex **3b**: ^1H NMR (CD_2Cl_2) *δ* 7.99 (d, $^3J = 5.3$ Hz, 1H), 7.43 (t*, $^3J = 7.8$ Hz, 1H), 6.89 (m, 2H), 6.19 (t*, $^3J = 6.2$ Hz, 1H), 4.98 (t*, $^3J = 6.1$ Hz, 1H), 4.42 (d, $^3J = 6.0$ Hz, 1H), 3.59 (d, $^3J = 7.3$ Hz, 1H), 0.45 (s, 1H, C*H*-$SiMe_3$), −0.15 (s, 9H, –$SiMe_3$) ppm. ^{13}C NMR (CD_2Cl_2, 0 °C) *δ* 235.1 (CrCO), 231.0 (MnCO), 229.0 (MnCO), 222.8 (MnCO), 159.0, 153.9, 138.8, 124.1, 119.0, 100.3, 93.6, 92.9, 91.5, 88.0, 87.5, 14.7, 0.9 ppm.

*4.8. Tricarbonyl[2-{tricarbonyl{1′,2′,3′,4′,5′,6′:η-2′-[(7′-methyl),(7′-phenyl)methylene-κC$^{7'}$]phenyl}chromium}-pyridine-κN]manganese (Cr,Mn) (**4a** and **4b**)*

Complex **1a** (300 mg, 0.66 mmol) in *n*-hexane (10 mL) and toluene (2 mL), (Me)(Ph)CN_2 (0.819 g, 6.2 mmol) in toluene (5 mL), reflux for 30 min. Chromatography on SiO_2 at 6 °C allowed the elution of a mixture of **4a**–**b** in a 1:3 ratio (210 mg, 60% yield) with a 9:1 mixture of CH_2Cl_2 and acetone. A second chromatographic purification with SiO_2 of smaller mesh was attempted at 1 °C in order to obtain a pure fraction of the major component of the mixture **4b**. Three fractions were eluted with 2:3, 7:3 and 9:1 mixtures of CH_2Cl_2 and *n*-hexane. Only the second fraction revealed the sole presence of complex **4b**, a dark red solid. The first fraction was basically a 1:1 mixture of **4a** and **4b**; the third fraction consisted of complex **4b** polluted by an unknown substance. Complex **4a**: ^1H NMR ($CDCl_3$) *δ* 7.89 (d, $^3J = 5.1$ Hz, 1H), 7.74 (m, 2H), 7.33 (m, 2H), 7.15 (m, 2H), 6.82 (m, 2H), 6.67 (d, $^3J = 8.1$ Hz, 1H), 4.48 (t*, $^3J = 6.0$ Hz, 1H), 4.35 (d, $^3J = 5.9$ Hz, 1H), 3.17 (d, $^3J = 7.8$ Hz, 1H), 1.66 (s, 3H) ppm. Complex **4b**: Elem. Anal. Calc. for $C_{25}H_{16}NO_6CrMn \cdot 1/3CH_2Cl_2$: C, 54.19; H, 2.97; N, 2.49. Found: C, 54.14; H, 3.25; N, 2.39%. HRMS calcd for $C_{25}H_{16}NO_6CrMn$ (EI): *m/e* 532.976. Found: 532.973. IR (CH_2Cl_2) *ν*(CO) 2007 (s), 1957 (s), 1925 (s), 1892 (m) cm^{-1}. ^1H NMR (CD_2Cl_2, 400 MHz, 263 K) *δ* 8.07 (d, $^3J = 7.6$ Hz, 1H), 7.77 (d, $^3J = 5.4$ Hz, 1H, H_{py}), 7.19 (d, $^3J = 7.8$ Hz, 1H, H_{Ph}), 7.03 (t, $^3J = 7.5$ Hz, 1H, H_{Ph}), 6.97 (t, $^3J = 7.7$ Hz, 1H, H_{py}), 6.91, (t, $^3J = 7.7$ Hz, 1H, H_{Ph}), 6.87 (t, $^3J = 7.2$ Hz, 1H, H_{Ph}), 6.52 (t, $^3J = 6.5$ Hz, 1H, H_{py}), 6.39 (t, $^3J = 6.1$ Hz, 1H, H_{Ph}), 6.24 (d, $^3J = 7.8$ Hz, 1H, H_{py}), 5.17 (t, $^3J = 6.8$ Hz, 1H, H_{ArCr}), 4.21 (d, $^3J = 6.1$ Hz, 1H, H_{ArCr}), 3.77 (d, $^3J = 7.7$ Hz, 1H, H_{ArCr}), 2.01 (s, 3H, –C*H*$_3$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, 223 K) *δ* 236.7 (CrCO), 235.5 (CrCO), 231.5 (CrCO), 231.1 (MnCO), 229.4 (MnCO), 220.2 (MnCO), 159.0, 152.3, 150.6, 137.4, 133.3, 130.4, 128.8, 127.7, 125.1, 122.6, 118.2, 97.5, 90.8, 89.6, 87.2,

84.7, 78.8, 42.8, 30.5 ppm. MS (EI): *m/e* 533 $[M]^+$, 449 $[M-3CO]^+$, 421 $[M-4CO]^+$, 393 $[M-5CO]^+$, 365 $[M-6CO]^+$, 310 $[M-6CO-Mn]^+$.

4.9. Tricarbonyl[2-{tricarbonyl{1′,2′,3′,4′, 5′,6′-η-2′-[(exo-7′-t-butyl),(endo-7′-phenyl)methylene-κC$^{7'}$]phenyl}chromium}pyridine-κN]manganese (Cr,Mn) (**5**)

Complex **1** (200 mg, 0.44 mmol) in toluene (15 mL), (Ph)(*t*-Bu)CN_2 (313 mg, 1.8 mmol) in toluene (3 mL), reflux 1 h. Chromatography on deactivated silica gel at +5 °C: elution of a purple band containing **5b** with a 7:3 mixture of CH_2Cl_2 and *n*-hexane. The product was recrystallised from CH_2Cl_2 and *n*-hexane (146 mg, 58% yield). Complex **5b**: Elem. Anal. Calc. for $C_{28}H_{22}NO_6CrMn$: C, 58.45; H, 3.85; N, 2.43. Found: C, 58.31; H, 3.88; N, 2.34%. IR (CH_2Cl_2) *ν*(CO) 2005 (s), 1952 (s), 1925 (s), 1893 (s) cm^{-1}. ^1H NMR ($CDCl_3$) *δ* 7.61 (d, $^3J = 5.1$ Hz, 1H), 7.45 (d, $^3J = 7.7$ Hz, 1H), 7.07 (d, $^3J = 7.9$ Hz, 1H), 6.86 (t*, $^3J = 7.5$ Hz, 1H), 6.73 (m, 3H), 6.38 (m, 2H), 5.58 (d, $^3J = 7.9$ Hz, 1H), 4.76 (t*, $^3J = 6.9$ Hz, 1H), 3.80 (m, 2H), 1.24 (s, 9H, C(CH_3)$_3$) ppm. ^{13}C NMR ($CDCl_3$) *δ* 235.3 (CrCO), 234.6 (MnCO), 230.7 (MnCO), 219.6 (MnCO), 161.8, 151.7, 147.3, 139.7, 137.3, 134.1, 127.8, 126.9, 125.0, 121.8, 117.0, 92.3, 89.1, 88.9, 87.3, 82.7, 79.3, 65.6, 39.5, 33.2 ppm.

4.10. Qualitative monitoring of the formation of **3a–b**

Complex **1a** (151 mg, 0.33 mmol) and 1,3,5-tri-*t*-butylbenzene (9.0 mg, 0.036 mmol) as internal reference were dissolved, boiled in a mixture of cyclohexane (15 mL) and toluene (1 mL), and mixed with (Me_3Si)(H)CN_2 (0.41 mL, 2 M, 0.82 mmol). Aliquots of ca. 1 mL were withdrawn from the reaction medium after 2.5, 5, 10, 15, 20, 25, 30 and 60 min of reaction. Each aliquot was evaporated to dryness, the residue dissolved in $CDCl_3$, the resulting mixture filtered through Celite to remove residual paramagnetic suspended solids and subsequently analyzed by ^1H NMR. Concentrations were calculated using the internal standard and by integrating several independent signals of complexes **3a** and **3b**.

4.11. Desilylation of **3a–b**

A 87:13 mixture of complexes **3a** and **3b** (0.096 g, 0.186 mmol) was dissolved in freshly distilled THF (11 mL). To this mixture was added a solution of 18/6 crown ether (0.099 g, 0.37 mmol) in THF (1 mL) and an aqueous solution (0.6 mL) of a mixture of KF (108 mg, 1.86 mmol) and [*n*-Bu_4N]Br. The resulting mixture was gently heated to ca. 55–60 °C for 24 h under an atmosphere of argon. The solvents were subsequently removed under reduced pressure and the residue was dissolved in CH_2Cl_2. Silica gel was added to this solution and the solvent was removed under reduced pressure. The coated silica gel was loaded on the top of a SiO_2 column packed in dry *n*-hexane at 5 °C. A first pale orange band containing **3c** was eluted with a 3:2 mixture of *n*-hexane and CH_2Cl_2, followed by a second red band containing **3a**, which was eluted with a 2:3 mixture of *n*-hexane and CH_2Cl_2. Two other, respectively, yellow and uncoloured fractions containing **3d** and **3e** were eluted with a 9:1 mixture of *n*-hexane and acetone. The removal of the solvents from each separated fraction allowed the recovery of **3c** (3 mg, 5% yield), **3a** (31 mg, 32% recovery), **3d** (10 mg, 26% yield) with an overall conversion of 68%. Complex **3a**: Elem. Anal. Calc. for $C_{21}H_{18}NO_6MnCrSi$: C, 48.94; H, 3.52; N, 2.72. Found: C, 48.43; H, 3.49; N, 2.69%. IR (CH_2Cl_2) *ν*(CO) 2008 (s), 1958 (s), 1922 (s), 1896 (w) cm^{-1}. ^1H NMR (CD_2Cl_2, 273 K, 500 MHz) *δ* 7.94 (d, $^3J = 4.9$ Hz, 1H), 7.41 (t, $^3J = 7.7$ Hz, 1H), 6.85 (m, 2H), 6.22 (t, $^3J = 6.0$ Hz, 1H), 4.85 (t, $^3J = 6.2$ Hz, 1H), 4.35 (d, $^3J = 5.9$ Hz, 1H), 3.51 (d, $^3J = 7.5$ Hz, 1H), 1.15 (s, 1H, $H_{benzylic}$), 0.26 (s, 9H, Me_3Si) ppm. ^{13}C NMR (CD_2Cl_2, 273 K, 125 MHz) *δ* 235.6 (CrCO), 231.8 (MnCO), 230.4 (MnCO), 222.0 (MnCO), 158.1, 152.7, 138.5, 123.4, 119.7, 99.1, 92.7, 90.9, 89.9, 86.5, 85.0, 21.1, 1.6 (Me_3Si) ppm. Complex **3c**, {2-{η^6-tetracarbonyl[1′(α-methylene-κC^α)phenyl]tricarbonylchromium(0)}-pyridine-κN}manganese (I): HRMS (FAB^+) calcd for $C_{34}H_{27}NMnO_3$: 470.924283. Found: 470.924283. IR (KBr) *ν*(CO) 2070 (w), 1988 (w), 1955 (vs), 1928 (s), 1876 (s), 1852 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 273 K, 500 MHz) *δ* 8.75 (d, $^3J = 5.7$ Hz, 1H), 7.86 (t*, $^3J = 7.6$ Hz, 1H), 7.63 (d, $^3J = 7.9$ Hz, 1H), 7.21 (t*, $^3J = 6.6$ Hz, 1H), 5.70 (d* + t*, 2H), 5.38 (d, $^3J = 6.5$ Hz, 1H), 5.15 (t*, $^3J = 6.4$ Hz, 1H), 2.06 (d, $^2J = 9.7$ Hz, 1H), 1.77 (d, $^2J = 9.6$ Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 273 K, 125 MHz) *δ* 233.5 (CrCO), 220.6 (MnCO), 213.9 (MnCO), 211.9 (MnCO), 158.5, 155.6, 139.5, 132.0, 126.1, 123.1, 100.0, 99.7, 96.9, 86.4, 85.5, 18.2 ppm. MS (FAB^+): *m/e* 471 $[M]^+$, 359 $[M-4CO]^+$, 331 $[M-5CO]^+$, 303 $[M-6CO]^+$, 223 $[M-6CO-Cr]^+$. Complex **3d**: Elem. Anal. Calc. for $C_{15}H_{11}NO_3Cr$: C, 59.02; H, 3.63; N, 4.59. Found: C, 58.92; H, 3.65; N, 4.52%. IR (CH_2Cl_2) *ν*(CO) 1966, 1896 cm^{-1}. ^1H NMR ($CDCl_3$, 283 K, 500 MHz) *δ* 8.61 (d, $^3J = 4.4$ Hz, 1H), 7.77 (t, $^3J = 8.3$ Hz, 1H), 7.57 (d, $^3J = 7.6$ Hz, 1H), 7.27 (m, 1H), 5.71 (d*, $^3J = 6.1$ Hz, 1H), 5.54 (t*, $^3J = 6.3$ Hz, 1H), 5.23 (d* + t*, 2H), 2.22 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 283 K, 125 MHz) *δ* 232.9 (CrCO), 155.3, 148.9, 136.9, 125.3, 123.0, 109.8 (2C), 97.5, 95.2, 92.2, 88.5, 19.9 ppm. Complex **3e**, 2-(2′-methylphenyl)pyridine: ^1H NMR ($CDCl_3$, 300 MHz) *δ* 8.74 (d, $^3J = 4.1$ Hz, 1H), 7.83 (t*, $^3J = 9.4$ Hz, 1H), 7.44 (d, $^3J = 7.6$ Hz, 2H), 7.31 (m, 4H), 2.38 (s, 3H) ppm.

4.12. Synthesis of 2-[tricarbonyl(η^6-o-tolyl)chromium]-pyridine **3d** from **3e**

Complex **3e** (200 mg, 0.26 mmol) was dissolved in dry tetrahydrofurane (15 mL) at −70 °C and treated with a *n*-hexane solution of *n*-BuLi (0.35 mL, 1.6 M, 0.57 mmol). The resulting yellow mixture was stirred for 30 min,

warmed to −20 °C and let to stand 4 h. The resulting dark red solution was treated with MeI (0.053 mL, 0.85 mmol), slowly warmed to room temperature and stirred overnight. The resulting solution was stripped from solvents under reduced pressure; the residue was dissolved in CH_2Cl_2 and filtered through basic alumina. The resulting light yellow solution was concentrated and *n*-hexane added in order to initiate the precipitation of **3d**, which was filtered off (55 mg, 35% yield) and recovered as a canary-yellow solid. Complex **3d**: Elem. Anal. Calc. for $C_{15}H_{11}NO_3Cr$: C, 59.02; H, 3.63; N, 4.59. Found: C, 58.92; H, 3.65; N, 4.52%. IR (CH_2Cl_2) *ν*(CO) 1966 (s), 1889 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 283 K) δ 8.60 (d, $^3J = 4.4$ Hz, 1H), 7.77 (m, 1H), 7.57 (d, $^3J = 7.6$ Hz, 1H), 7.27 (m, 1H), 5.71 (m, 1H), 5.54 (t*, $^3J = 6.3$ Hz, 1H), 5.23 (m, 2H), 2.22 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 283 K) δ 232.9 (CrCO), 155.2, 149.4, 148.9, 136.9, 125.3, 123.0, 120.0, 109.8, 97.5, 95.2, 92.2, 91.7, 88.5, 19.9 ppm.

*4.13. Tricarbonyl[2-tricarbonyl{η⁶-{1′-[(endo-1-phenyl),(3-ferrocenyl)propylene- κC1]phenyl}chromium(0)}-3-methylpyridine-κN]manganese (I) (**6b**)*

Under argon, **1b** (120 mg, 0.25 mmol) in a 1:1 mixture of heptane (4 mL) and toluene (4 mL), reflux. Addition of a solution in toluene (3 mL) of 1-diazo,3-ferrocenyl,1-phenyl,propane (318 mg, 0.96 mmol), over 15 min.; additional stirring for 45 min. Flash chromatography on SiO_2 at 274 K elution with a 4:1 mixture of dichloromethane with *n*-hexane afforded a red band (150 mg, 79% conversion) consisting of a mixture of **6a** and **6b** isomers in a 1:6.7 ratio. A second chromatography carried out with this mixture allowed the isolation of pure **6b** by elution with a 1:1 mixture of dichloromethane and *n*-hexane (60 mg, 32% yield) and again a 1:6 mixture of **6a** and **6b** in a second fraction eluted with a 3:1 mixture of dichloromethane and *n*-hexane (70 mg, 37% yield). Complex **6b**: Elem. Anal. Calc. for $C_{37}H_{28}NO_6CrFeMn \cdot 1/2CH_2Cl_2$: C, 58.36;H, 3.75; N, 1.83. Found: C, 58.24; H, 3.76; N, 1.89%. IR (CH_2Cl_2) *ν*(CO) 2006 (vs), 1956 (s), 1923 (m), 1893 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 263 K, 500 MHz) δ 7.99 (d, $^3J = 7.3$ Hz, 1H, H_{Ph}), 7.68 (d, $^3J = 5.4$ Hz, 1H, H_{py}), 7.21 (d, $^3J = 7.8$ Hz, 1H, H_{Ph}), 7.00 (t* + t*, 2H, H_{Ph}), 6.89 (t*, $^3J = 7.3$ Hz, 1H, H_{Ph}), 6.67 (d, $^3J = 7.8$ Hz, 1H, H_{py}), 6.35 (t, $^3J = 6.6$ Hz, 1H, H_{PhArCr}), 6.26 (t, $^3J = 6.0$ Hz, 1H, H_{Py}), 4.90 (t, $^3J = 6.8$ Hz, 1H, H_{PhArCr}), 4.10 (d, $^3J = 6.1$ Hz, 1H, H_{PhArCr}), 3.98 (m, 8H, H_{Fc}), 3.92 (m, 1H, H_{Fc}), 3.56 (d, $^3J = 7.0$ Hz, 1H, H_{PhArCr}), 2.76 (m, 1H, $H_{CH2–CH2}$), 2.44 (m, 2H, $H_{CH2–CH2}$), 2.19 (m, 1H, $H_{CH2–CH2}$), 1.78 (s, 3H, H_{Me}) ppm. ^{13}C NMR ($CDCl_3$, 263 K, 125 MHz) δ 237.2 (CrCO), 235.0 (CrCO), 232.1 (CrCO), 231.9 (MnCO), 229.3 (MnCO), 220.1 (MnCO), 156.9, 150.1, 147.6, 139.9, 133.2, 131.4, 129.7, 129.0, 126.8, 125.4, 121.9, 98.4 (C_{PhCr}), 90.0 (C_{PhCr}), 88.9 (C_{PhCr}), 88.0 (C_{PhCr}), 87.9 (C_{PhCr}), 85.9 (C_{PhCr}), 78.3 (1C, C_{Cp}), 68.5 (5C, C_{Cp}), 68.0 (1C, C_{Cp}), 67.7 (1C, C_{Cp}), 67.2 (1C, C_{Cp}), 67.1 (1C, C_{Cp}), 49.8, 43.1, 27.4, 20.2 ppm.

Acknowledgements

The authors gratefully acknowledge the CNRS for financial support and Dr. Zoran Ratković (University of Kragujevac, Serbia) for his contribution to this work.

Appendix A. Supplementary data

Complete crystallographic data for the structures of compounds **2c**, **3a**, **3c**, **4b**, **5b** and **6b** have been deposited as CIFs with the Cambridge Structural Database under reference numbers CCDC Nos. 270304–270309. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.10.029.

References

[1] (a) L. Pauling, The Nature of the Chemical Bond, Cornell University, Ithaca, NY, 1960;
(b) A. Bondi, J. Phys. Chem. 68 (1964) 441–451;
(c) A. Bondi, J. Phys. Chem. 70 (1966) 3006–3007;
(d) S.S. Batsanov, J. Mol. Struct. (Theochem.) 468 (1999) 151–159;
(e) S.S. Batsanov, Inorg. Mater. 37 (2001) 871–885, and references therein.

[2] (a) A.A. Hock, O.S. Mills, Acta Crystallogr. 14 (1961) 139–148;
(b) R.D. Barr, M. Green, K. Marsden, F.G.A. Stone, P. Woodward, J. Chem. Soc., Dalton Trans. (1983) 507–512.

[3] J.P. Djukic, A. Maisse, M. Pfeffer, K.H. Dötz, M. Nieger, Eur. J. Inorg. Chem. (1998) 1781–1790.

[4] J.P. Djukic, A. Maisse-François, M. Pfeffer, K.H. Dötz, A. De Cian, J. Fischer, Organometallics 19 (2000) 5484–5499.

[5] J.P. Djukic, K.H. Dötz, M. Pfeffer, A. De Cian, J. Fischer, Organometallics 16 (1997) 5171–5182.

[6] (a) R.M. Bullock, C.P. Casey, Acc. Chem. Res. 20 (1987) 167–173;
(b) S. Töfke, U. Behrens, J. Organomet. Chem. 338 (1988) 29–45.

[7] (a) F.W.B. Einstein, R.K. Pomeroy, P. Rushman, A.C. Willis, Organometallics 4 (1985) 250–255;
(b) L.W. Arndt, M.Y. Darensbourg, T. Delord, B. Trzcinska-Bancroft, J. Am. Chem. Soc. 108 (1986) 2617–2627;
(c) F.W.B. Einstein, M.C. Jennings, R. Krentz, R.K. Pomeroy, P. Rushman, A.C. Willis, Inorg. Chem. 26 (1987) 1341–1344;
(d) H.B. Davis, F.W.B. Einstein, P.G. Glavina, T. Jones, R.K. Pomeroy, P. Rushman, Organometallics 8 (1989) 1030–1039;
(e) R.J. Batchelor, H.B. Davis, F.W.B. Einstein, R.K. Pomeroy, J. Am. Chem. Soc. 112 (1990) 2036–2037.

[8] (a) V.N. Kalinin, I.A. Cherepanov, S.K. Moiseev, A.S. Batsanov, Yu.T. Struchkov, Mendeleev Commun. (1991) 77–78;
(b) V.N. Kalinin, I.A. Cherepanov, S.K. Moiseev, F.M. Dolgushin, A.I. Yanovski, Yu.T. Struchkov, Acta Crystallogr., Sect. C 49 (1993) 805–808;
(c) S.K. Moiseev, I.A. Cherepanov, P.V. Petrovskii, M.G. Ezernitzkaya, H. Butenschön, M. Strotmann, V.N. Kalinin, Inorg. Chim. Acta 280 (1998) 71–74.

[9] J.P. Djukic, M. Pfeffer, K.H. Dötz, C.R. Acad. Sci. Paris, T.2, Série IIc (1999) 403–408.

[10] (a) C. Bonifaci, A. Ceccon, A. Gambaro, P. Ganis, S. Santi, G. Valle, A. Venzo, Organometallics 12 (1993) 4211–4214;
(b) C. Bonifaci, A. Ceccon, A. Gambaro, P. Ganis, S. Santi, G. Valle, A. Venzo, J. Organomet. Chem. 492 (1995) 35–39;
(c) C. Bonifaci, G. Carta, A. Ceccon, A. Gambaro, S. Santi, A. Venzo, Organometallics 15 (1996) 1630–1636;
(d) P. Cecchetto, A. Ceccon, A. Gambaro, S. Santi, S. Ganis, R. Gobetto, G. Valle, A. Venzo, Organometallics 17 (1998) 752–762.

[11] S.P. Tunik, P.N. Shipil, A.V. Vlasov, V.R. Denisov, A.B. Nikol'skii, F.M. Dolgushin, A.I. Yanovsky, Yu.T. Struchkov, J. Organomet. Chem. 515 (1996) 11–17.
[12] H. Nakatsuji, M. Hada, A. Kawashima, Inorg. Chem. 31 (1992) 1740–1744.
[13] (a) P. Macchi, D.M. Proserpio, A. Sironi, J. Am. Chem. Soc. 120 (1998) 13429–13435;
(b) R. Bianchi, G. Gervasio, D. Marabello, Inorg. Chem. 39 (2000) 2360–2366;
(c) R. Llusar, A. Beltran, J. Andres, F. Fuster, B. Silvi, J. Phys. Chem. A 105 (2001) 9460–9466.
[14] (a) J.P. Djukic, C. Michon, A. Maisse-François, R. Allagapen, M. Pfeffer, K.H. Dötz, A. de Cian, J. Fischer, Chem. Eur. J. 6 (2000) 1064–1070;
(b) C. Michon, J.P. Djukic, Z. Ratkovic, J.P. Collin, M. Pfeffer, A. de Cian, J. Fischer, D. Heiser, K.H. Dötz, M. Nieger, Organometallics 21 (2002) 3519–3535;
(c) C. Michon, Ph.D. Dissertation, Université Louis Pasteur, Strasbourg, 2003.
[15] J.P. Djukic, C. Michon, D. Heiser, N. Kyritsakas-Gruber, A. de Cian, K.H. Dötz, M. Pfeffer, Eur. J. Inorg. Chem. (2004) 2107–2122.
[16] (a) M.I. Bruce, M.J. Liddell, M.R. Snow, E.R.T. Tiekink, Aust. J. Chem. 41 (1988) 1407–1415;
(b) R.L. Bennett, M.I. Bruce, I. Matsuda, R.J. Doedens, R.G. Little, J.T. Veal, J. Organomet. Chem. 67 (1974) C72–C74.
[17] A.J. Arduengo, H.V.R. Dias, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 114 (1992) 5530–5534.
[18] K.H. Dötz, H. Fischer, P. Hofmann, F.R. Kreißl, U. Schubert, K. Weiss, Transition Metal Carbene Complexes, Verlag Chemie, Weinheim, 1983.
[19] According to the recommendations of the IUPAC, the stereochemistry of the octahedral Mn(I) fragment can be defined by its related *OC* descriptor; therefore if the ligands bonded to Mn have the following priority: (1) N; (2) C_{ArCr}; (3) $C_{alkylidene}$; (4) CO and if the N–Mn–CO axis is the principal axis, the resulting stereochemical descriptor for this *fragment* is [*OC*-6-42]. Moreover, for either enantiomer of **2c**, a *chirality symbol* can be defined. Considering the principal axis defined above and the priority order defined for the Mn-bound ligands, the chirality symbol that is obtained is *A* (anticlockwise) for the (p*S*) enantiomer of **2c** and conversely C (clockwise) for the (p*R*) enantiomer. To simplify the perception of the stereochemistry of **2c** and in order to explicit even more the stereochemical relationship between the chiral manganese center and the planar chiral aryl group bonded to the chromium, it is proposed that facial CO ligands be considered equally as one ligand with priority number (4). This being assumed, one can define a configuration at Mn thus extending the Cahn–Ingold–Prelog rule: consequently **2c** can be considered as a racemate of *l* (like) diastereomers having, respectively, (p*S*, S_{Mn}) –(p*S*-[*OC*-6-42*A*])– and (p*R*,R_{Mn}) –(p*S*-[*OC*-6-42*C*])– configurations; note that the *u* (unlike) isomers would have the alkylidene ligand in a *syn* relationship with the $Cr(CO)_3$ fragment entailing therefore (p*S*,R_{Mn}) and (p*R*,S_{Mn}) configurations. For references: G.J. Leigh (Ed.) in Nomenclature of Inorganic Chemistry, Recommendations 1990: IUPAC, Blackwell Scientific Publications, Oxford, 1990.
[20] (a) W.A. Herrmann, L.J. Goosen, C. Kocher, G.R.J. Artus, Angew. Chem., Int. Ed. Engl. 35 (1996) 2805–2807;
(b) W.A. Herrmann, L.J. Goossen, G.R.J. Artus, C. Kocher, Organometallics 16 (1997) 2472–2477;
(c) M. Tafipolsky, W. Scherer, K. Ofele, G. Artus, B. Pedersen, W.A. Herrmann, G.S. McGrady, J. Am. Chem. Soc. 124 (2002) 5865–5880;
(d) C. Bolm, M. Kesselgruber, G. Raabe, Organometallics 21 (2002) 707–710.
[21] G.L. Closs, J.J. Coyle, J. Org. Chem. 31 (1966) 2759–2765.
[22] (a) K. Ishiguro, M. Ikeda, Y. Sawaki, J. Org. Chem. 57 (1992) 3057–3066;
(b) D.E. Pearson, J. Am. Chem. Soc. 72 (1950) 4169–4170.
[23] A. Berger, A. de Cian, J.P. Djukic, J. Fischer, M. Pfeffer, Organometallics 20 (2001) 3230–3240.
[24] J.P. Djukic, F. Rose-Munch, E. Rose, J. Vaissermann, Eur. J. Inorg. Chem. (2000) 1295–1306.
[25] J.P. Djukic, A. Maisse, M. Pfeffer, J. Organomet. Chem. 567 (1998) 65–74.
[26] C.K. Fair, MolEN: An Interactive Intelligent System for Crystal Structure Analysis, Nonius, Delft, The Netherlands, 1990.
[27] G.M. Sheldrick, SHELXL-97: Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997.
[28] (a) J. Federic, S. Toma, Coll. Czech. Chem. Commun. 52 (1987) 174–181;
(b) T.A. Mashburn, C.E. Cain, C.R. Hauser, J. Org. Chem. 25 (1960) 1982–1986.