First Synthesis and Structural Characterization of Neutral Chelated *syn*-Facial Bimetallic (η^5-Cyclohexadienyl)benzylidene Complexes from Tetracarbonyl[2-{(η^6-phenyl)tricarbonylchromium(0)-$\kappa C^{2'}$}pyridine-κN]manganese(I) Derivatives

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Reaction of tetracarbonyl[2-{(η^6-phenyl)tricarbonylchromium-$\kappa C^{2'}$}pyridine-κN]manganese(I), **2a**, with phenyllithium quantitatively affords an acylmanganese anion **3a** that can be isolated and spectroscopically characterized. In-situ *O*-alkylation of the latter anion by means of $MeOSO_2CF_3$ at low temperature, yields a new neutral *syn*-facial heterobimetallic analog **4a** of (η^5-cyclohexadienyl)-benzylidene complexes. The treatment of bimetallic carbonyl complexes of 3-methyl, 2-phenyl-pyridine and 2-phenylquinoline, **2b** and **2c**, with PhLi and subsequently with $MeOSO_2CF_3$ affords deep purple crystalline products **4b** and **4c** that have been structurally characterized by X-ray diffraction analyses. The molecular structures of **4b** and **4c** display, among other features, an overall helical shape with a pronounced π-stacking of the aromatic groups and a weak interaction between the chromium and the manganese centered units.

Introduction

We recently reported that cyclomanganated 2-phenylpyridine derivatives undergo a nucleophilic attack at a coordinated carbonyl ligand upon treatment with aryllithium reagents[1]. ^{13}C-NMR and IR spectroscopic measurements have revealed the formation of anionic acylmetalate intermediates which were shown to be prone either to decomposition by a reductive elimination process when kept in a solution at ambient temperature or to conversion into new chelated η^3-benzylic manganese complexes upon alkylation with $MeOSO_2CF_3$. These results demonstrated that chelated octahedral (tetracarbonyl)manganese(I) complexes display a reactivity toward organolithium reagents similar to that of the widely studied hexacarbonylmetal complexes of the chromium triade[2]. To our knowledge, this constituted the first report for a non-oxidative chemical transformation producing a new class of organomanganese compounds from cyclomanganated substrates[3]. In our continuing efforts to find new reactivity patterns for cyclomanganated aromatics we were naturally lead to study the behaviour of the peculiar class of chelated complexes derived from (η^6-arene)tricarbonylchromium complexes[4]. We[4a][4b] and other authors[4c] did previously report that such bimetallic complexes can be readily synthesized in preparative scale. Some examples have been used in the stereoselective insertion reactions of alkynes leading to π-coordinated indenol complexes[4c]. Herein, we report that the addition of phenyllithium to cyclomanganated 2-[(η^6-phenyl)-tricarbonylchromium]pyridine yields an air- and temperature-sensitive acylmanganate intermediate. Further alkylations of this and other analogous anionic intermediates afford novel neutral chelated *syn*-facial heterobimetallic (η^5-cyclohexadienyl)benzylidene complexes in which the two metallic centers, e.g. chromium and manganese, are involved in a weak metal−metal interaction that resembles a metal−metal dative bond[5].

Results and Discussion

1. Synthesis of Chelated Bimetallic (η^5-Cyclohexadienyl)benzylidene Complexes 4a−c

The reaction of an orange solution of complex **2a** with 1 equiv. of phenyllithium in DME[6] at −50°C yielded within

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seconds a dark brown solution containing the acylmanganate **3a**-Li (Scheme 1). In order to properly characterize this reaction product we isolated the latter and exchanged the lithium cation for the more bulky PPN$^+$ counter cation. The $^{13}C\{^1H\}$-NMR analysis of the resulting compound, e.g. **3a**-PPN, confirmed the presence of only one product. In the carbonyl ligand resonance region we detected singlets at δ = 219.7, 222.9, and 231.1 that we assigned to the ^{13}C resonances of the $Mn(CO)_3$ group, an intense signal at δ = 237.5 produced by the carbonyl ligands of the $Cr(CO)_3$ moiety and a downfield singlet at δ = 289.5 attributed to the acyl carbon of the benzoyl group located on the manganese center. From this spectrum it was clear that the nucleophilic attack did not take place at a carbonyl ligand of the $Cr(CO)_3$ moiety but rather selectively at a CO ligand located on the manganese center. Similar chemical shifts for the carbonyl ligands of the $Mn(CO)_3$ group were previously obtained for lithium (benzoyl)(tricarbonyl)[2-(phenyl-κ*C*$^{2'}$), pyridine-κ*N*]manganate(I)[1].

The infrared spectrum of **3a**-PPN in CH_2Cl_2 displays three intense absorption bands at 1972, 1930, and 1847 cm^{-1}, a shoulder at 1878 cm^{-1} and a weak band at 1560 cm^{-1} that may be assigned to as the C−O streching vibration of the benzoyl group. The former set of three intense signals can be considered reasonably as the result of the overlap of the two sets of A_1+E vibration modes related to the *fac*-$L_3Cr(CO)_3$ group and to a *fac*-$L_3Mn(CO)_3$ moiety. A *mer*-$L_3Mn(CO)_3$ moiety resulting from a nucleophilic attack at an equatorial CO ligand would have given three distinct absorption bands, e.g. $2A_1+B_2$, with the two A_1 vibration modes showing up at the higher frequencies[7].

Analogous anionic intermediates can be prepared starting from **2b** and **2c** by reaction with PhLi under experimental conditions similar to those used for the formation of **3a**-Li. In situ alkylation of the anionic adducts originating from **2a**−**c** at −20°C with $MeOSO_2CF_3$ gave rise to a dramatic change in colour of the reaction mixture from dark brown to dark red. Isolation of the corresponding reaction products afforded after chromatographic purification, the complexes **4a**, **4b**, and **4c** in 67, 70 and 45% yield respectively (based on the starting bimetallic substrates).

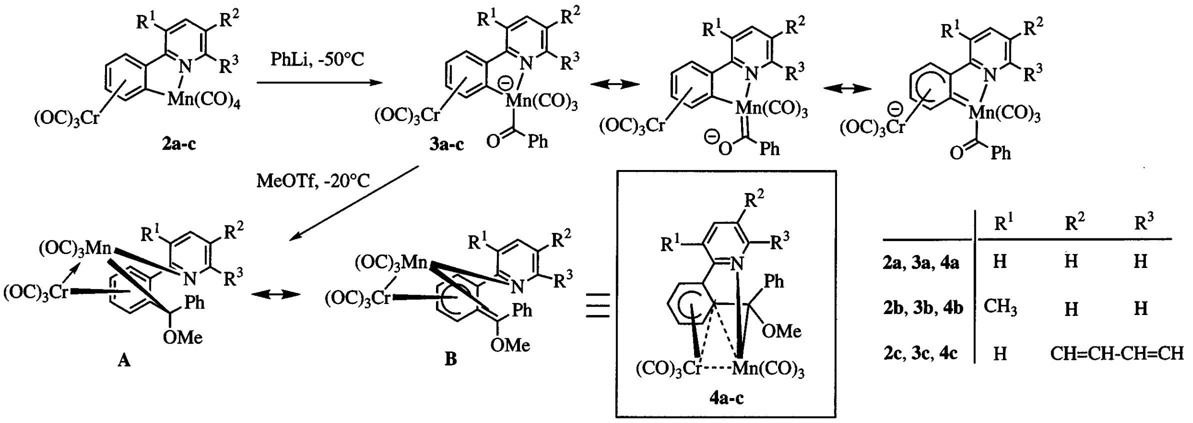
2. Molecular Structures of Complexes 4b and 4c

Crystallization of compounds **4b** (Figure 1) and **4c** (Figure 2) from mixtures of dichloromethane and hexane at −18°C afforded crystals suitable for X-ray crystal structure analysis. Details of data collection and refinement are summarized in Table 3. Selected interatomic distances, bond angles and torsion angles are given in Table 1 for compound **4b** and in Table 2 for compound **4c**.

The two molecules represented in Figures 1 and 2 reveal a quite compact intramolecular arrangement. Both metal-carbonyl fragments are coordinated to the same face of the organic ligand and the carbonyl ligands occupy positions that minimize steric interactions. The average Cr−Mn distance of 3.03 Å indicates interaction between what may be considered a formally closed shell 18 electron chromium(0) center and an electron-deficient 16 electron manganese(I) center. Obviously, the electron bookkeeping for each metal and the transcription of the relevant formulae rise several questions. At first glance, resonance forms depicted for **4a−c** in Scheme 1 have different chemical meanings[8]. The formula denoted as **A** includes a dative bond between the two metals whereas **B**, includes a single covalent bond. A choice between these two formulations must rely at least on thorough theoretical investigations that are not available so far for the type of bridging ligand described here. To our knowledge, only a few theoretical studies are available on donor-acceptor or dative transition metal-metal interactions involving[9] or not[10] bridging ligands. This ambiguity was already addressed for other bimetallic compounds that fit neither of the two aforementioned metal to metal interaction types[11]. At this stage of our study, we chose an intermediate "dashed bond" formulation for the molecular structures of **4a−c** which emcompasses the main structural informations extracted from the two available molecular structures (vide infra). In this formulation, the dashed lines indicate interactions of uncertain nature.

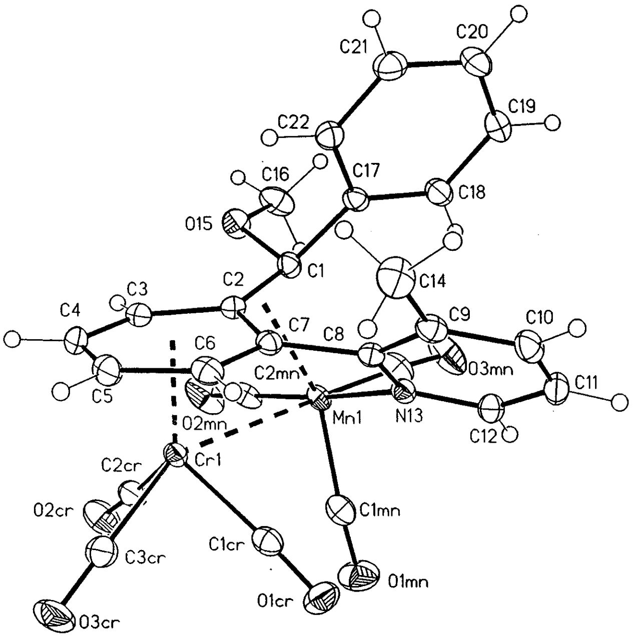
A close analysis of the metal-centered bond angles for the chelated $Mn(CO)_3$ fragment indicates that in both **4b** and **4c** the manganese atom is located in a slightly distorted octahedral coordination geometry (Tables 1 and 2). In this

Scheme 1



	R1	R2	R3
2a, 3a, 4a	H	H	H
2b, 3b, 4b	CH_3	H	H
2c, 3c, 4c	H	CH=CH-CH=CH	

Figure 1. ORTEP diagram and atom numbering scheme of the molecular structure of **4b**. Ellipsoids are scaled to enclose 30% of the electronic density



configuration the chromium atom, the pyridyl or quinolinyl group, and two carbonyl ligands occupy four equatorial positions, the two axial positions being held by the pseudo-benzylic carbon C(1) and by the third carbonyl ligand. The pseudo-benzylic and heterocyclic rings connected through C(7)−C(8) are twisted around this axis by about 45° [torsion angle C(2)−C(7)−C(8)−N(13) for **4b**: −42.9(2)°, for **4c**: 137.38(19)°] which is about 5° more than that observed for the mononuclear analog **5**[1].

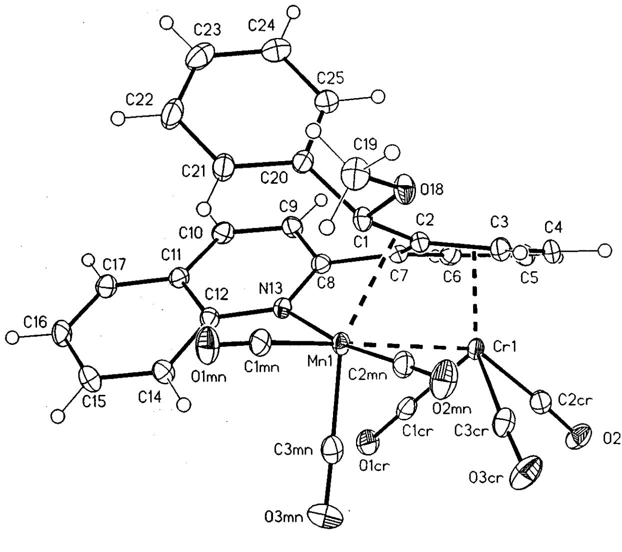
The geometry of the $Cr(CO)_3$ moiety does not change dramatically from that commonly observed in (η^6-arene)-tricarbonylchromium complexes. The two chromium-bound CO ligands that are oriented towards the manganese center form a OC−Cr−CO bond angle of approximately 96° which may be considered intermediate between the average value of 89° generally observed in common (η^6-arene)tricarbonylchromium complexes[12] and the value of 105° for neutral tricarbonyl(η^5-cyclohexadienyl)(triphenyltin)chromium(*Cr-Sn*) complexes[13]. This relatively wide angle reflects not only a steric hindrance but also some peculiar bonding interactions between the chromium center and its surrounding ligands[14].

We reported previously[1] that in complex **5** the manganese center was more likely bound to the benzylic ligand through a η^1:η^2 bonding mode rather than via an ideal symmetric η^3 allylic-like mode. This conclusion was based on the analysis of the metal-to-carbon atom distances. The shortest distance of 2.104(4) Å was obtained for the pseudo-benzylic carbon-to-Mn bond, C1−Mn (Scheme 2), and the longest distance of 2.438(4) Å for the *ipso*-aromatic carbon-to-Mn bond C7−Mn (Scheme 2).

Table 1. Selected bond lengths, angles, and torsion angles for **4b**

Bond lengths [Å]		Bond angles [deg]	
Mn(1)−C(3Mn)	1.769(2)	C(1)−Mn(1)−Cr(1)	86.20(5)
Mn(1)−C(2Mn)	1.8129(19)	C(2)−Mn(1)−Cr(1)	49.76(4)
Mn(1)−C(1Mn)	1.8249(19)	C(7)−Mn(1)−Cr(1)	44.00(3)
Mn(1)−C(1)	2.1493(17)	N(13)−Mn(1)−Cr(1)	85.03(4)
Mn(1)−C(2)	2.4034(18)	C(1Mn)−Mn(1)−Cr(1)	90.86(6)
Mn(1)−C(7)	2.9401(18)	C(2Mn)−Mn(1)−Cr(1)	92.65(6)
Mn(1)−Cr(1)	3.0336(4)	C(3Mn)−Mn(1)−Cr(1)	178.06(6)
Cr(1)−C(3Cr)	1.8394(19)	C(1)−Mn(1)−C(2)	36.67(6)
Cr(1)−C(1Cr)	1.8595(19)	O(15)−C(1)−C(17)	109.64(13)
Cr(1)−C(2Cr)	1.870(2)	C(1Cr)−Cr(1)−C(3Cr)	82.59(8)
Cr(1)−C(5)	2.1891(18)	C(3Cr)−Cr(1)−C(2Cr)	82.76(9)
Cr(1)−C(4)	2.2112(18)	C(1Cr)−Cr(1)−C(2Cr)	97.52(8)
Cr(1)−C(6)	2.2125(17)		
Cr(1)−C(3)	2.2308(17)	Torsion angles [deg]	
Cr(1)−C(7)	2.2396(16)	C(1)−C(2)−C(7)−C(8)	−16.4(2)
Cr(1)−C(2)	2.3576(17)	C(6)−C(7)−C(8)−C(9)	−47.1(2)
C(1)−O(15)	1.429(2)	C(2)−C(7)−C(8)−N(13)	−42.9(2)
C(1)−C(2)	1.452(2)		
C(1)−C(17)	1.522(2)		
C(2)−C(3)	1.437(2)		
C(2)−C(7)	1.454(2)		
C(3)−C(4)	1.392(2)		
C(4)−C(5)	1.410(3)		
C(5)−C(6)	1.414(3)		
C(6)−C(7)	1.405(2)		
C(7)−C(8)	1.490(2)		
C(1Cr)−O(1Cr)	1.153(2)		
C(2Cr)−O(2Cr)	1.146(2)		
C(3Cr)−O(3Cr)	1.154(2)		
C(16)−O(15)	1.424(2)		

Figure 2. ORTEP diagram and atom numbering scheme of the molecular structure of **4c**. Ellipsoids are scaled to enclose 30% of the electronic density



In **4b** and **4c** the corresponding average Mn(1)−C(7) bond distance of 2.91 Å is beyond the range of generally accepted C−Mn bond lengths of either σ- or π-coordinated carbon atoms[15]. The Mn(1)−C(2) (2.40 Å and 2.36 Å) and Mn(1)−C(1) (2.15 Å) are consistent with an altered π-type coordination between Mn(1), C(1), and C(2) even though the C(1)−C(2) bond distance of 1.45 Å in **4b** and **4c** is longer than that of a typical metal-coordinated C=C bond. This is supported by the fact that amongst all the aromatic

Table 2. Selected bond lengths, angles, and torsion angles for **4c**

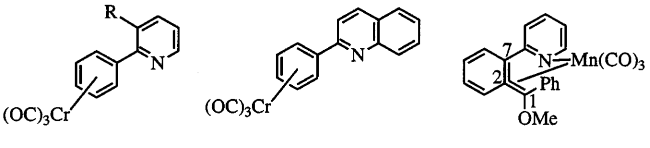
Bond lengths [Å]		Bond angles [deg]	
Mn(1)−C(3Mn)	1.8339(16)	C(1)−Mn(1)−Cr(1)	87.81(4)
Mn(1)−C(2Mn)	1.8000(16)	C(2)−Mn(1)−Cr(1)	50.71(3)
Mn(1)−C(1Mn)	1.7759(16)	C(7)−Mn(1)−Cr(1)	44.09(3)
Mn(1)−C(1)	2.1494(15)	N(13)−Mn(1)−Cr(1)	85.78(3)
Mn(1)−C(2)	2.3619(14)	C(1Mn)−Mn(1)−N(13)	98.52(6)
Mn(1)−C(7)	2.8908(15)	C(2Mn)−Mn(1)−Cr(1)	91.07(6)
Mn(1)−Cr(1)	3.0444(3)	C(3Mn)−Mn(1)−Cr(1)	85.89(5)
Cr(1)−C(3Cr)	1.8713(17)	C(1)−Mn(1)−C(2)	37.29(6)
Cr(1)−C(1Cr)	1.8637(16)	C(20)−C(1)−O(18)	111.68(11)
Cr(1)−C(2Cr)	1.8479(16)	C(2Cr)−Cr(1)−C(1Cr)	84.26(7)
Cr(1)−C(5)	2.1972(15)	C(2Cr)−Cr(1)−C(3Cr)	81.90(6)
Cr(1)−C(4)	2.2203(15)	C(1Cr)−Cr(1)−C(3Cr)	94.96(7)
Cr(1)−C(6)	2.2180(15)		
Cr(1)−C(3)	2.2460(15)	Torsion angles [deg]	
Cr(1)−C(7)	2.2323(14)	C(1)−C(2)−C(7)−C(8)	−16.3(2)
Cr(1)−C(2)	2.3957(14)	C(9)−C(8)−C(7)−C(2)	−45.5(2)
C(1)−O(18)	1.4263(18)	C(6)−C(7)−C(8)−C(9)	−45.5(2)
C(1)−C(2)	1.456(2)	C(3)−C(2)−C(7)−C(6)	−13.7(2)
C(1)−C(20)	1.517(2)	C(2Mn)−Mn(1)−Cr(1)−C(3Cr)	33.40(7)
C(2)−C(3)	1.437(2)	C(3Mn)−Mn(1)−Cr(1)−C(3Cr)	−56.83(7)
C(2)−C(7)	1.446(2)	C(3Mn)−Mn(1)−Cr(1)−C(1Cr)	41.57(7)
C(3)−C(4)	1.394(2)	C(2)−C(7)−C(8)−N(13)	137.38(19)
C(4)−C(5)	1.415(3)		
C(5)−C(6)	1.411(3)		
C(6)−C(7)	1.409(2)		
C(7)−C(8)	1.481(2)		
C(1Cr)−O(1Cr)	1.1472(19)		
C(2Cr)−O(2Cr)	1.1527(19)		
C(3Cr)−O(3Cr)	1.151(2)		
C(19)−O(18)	1.4202(19)		

carbon atoms bound to the chromium, C(2) is the farthest with an average Cr(1)−C(2) bond distance for **4b** and **4c** of 2.38 Å as compared to the remainder average Cr(1)−C_{Ar} bond distance of 2.22 Å. A reasonable compromise to describe the coordination mode of atom C(2) is to present it as a part of a multicenter bonding system (Scheme 1).

The asymmetric bonding mode of the arene can be well characterized by the angle θ defined as the angle formed between the mean planes C(3)−C(2)−C(7) and C(3)−C(4)−C(5)−C(6)−C(7) in complexes **4b−c**. The calculation of the least square planes indicated no major deviation from the plane for C(5). The calculated values of θ were 8.3° for **4b** and 11.0° for **4c**. In other terms the structural features of the coordinated arene rather confirm a quasi η^5-coordination to the $Cr(CO)_3$ group[16].

As previously underlined for complex **5** (Scheme 2), compounds **4b** and **4c** possess a marked helicity characterized by the overlying of the aromatic rings originating from the N-heterocycles and the phenyl group attached to C(1). In the compounds described herein, the spacial arrangement of the aromatic rings implies relevant geometric distortions of the coordinated arene. Indeed, atoms C(1) and C(8) are forced in opposite directions with respect to the mean plane of the chromium-coordinated arene ring [C(1) towards the uncomplexed arene ring and C(8) towards manganese]. This distortion is evident in both complexes as the torsion angle C(1)−C(2)−C(7)−C(8) amounts 16°.

Scheme 2



1a, R= H
1b, R= Me
1c
5

3. Spectroscopic Properties of Complexes 4a−c

The infrared spectra of compounds **4a−c** present four different signals at approximate frequencies of 2010 (sharp and strong), 1960 (strong), 1924 (medium and broad), and 1890 (medium and broad) cm^{-1} in CH_2Cl_2. This pattern is consistent with the overlap of two A_1+E vibration modes patterns of the *fac*-$Cr(CO)_3$ (1960 and 1890 cm^{-1}) and *fac*-$Mn(CO)_3$ (2010 and 1924 cm^{-1}) fragments, respectively.

A rough comparison of the frequency of the E mode absorption band produced by the chromium tripod in **4a−c** with that of the simple monometallic complexes **1a−c** (Scheme 2) informs about the magnitude of the electron density exchange between the manganese and the chromium atoms. For instance, if we consider both complexes **1a** (Scheme 2) and **4a**, the absorption band arising from the E vibration mode of the $Cr(CO)_3$ fragment undergoes a relative bathochromic shift $\Delta\nu_E$ ($\Delta\nu_E = \nu_{E\mathbf{1a}} - \nu_{E\mathbf{4a}}$) upon intimate interaction with the $L_2Mn(CO)_3$ moiety of about 10 cm^{-1} suggesting an electron density transfer from the manganese to the chromium center. Similar values can be calculated for the couples **1b**/**4b** and **1c**/**4c**. It must be pointed out that the value of Dn_E is only a rough estimation since the coordinated arenes in **1a**/**4a** are slightly different in nature.

A more reliable comparative study can be based on the carbonyl ligand absorptions of complexes **4a** and **5** that differ by the absence of the $Cr(CO)_3$ moiety in the latter compound[1]. One may consider the A_1 absorption bands of the $Mn(CO)_3$ fragment that are detected at 2000 cm^{-1} in CH_2Cl_2 for **5** and at 2010 cm^{-1} in CH_2Cl_2 for **4a**. A new bathochromic shift value can be defined as

$$\Delta\nu_{Cr} = \nu_{Mn-Cr} - \nu_{Mn},$$

with ν_{Mn} defining the frequency of the A_1 mode band in the η^3-benzyl manganese complex **5** and ν_{Mn-Cr} designing the corresponding A_1 mode band in the *syn*-facial heterobimetallic compound **4a**. The difference of 10 cm^{-1} obtained for **5** and **4a** confirms a loss of electron density on the Mn-centered fragment as a consequence of the concomittant interaction with the $Cr(CO)_3$ moiety and structural rearrangements of the molecule. A similar effect of 8 cm^{-1} for $\Delta\nu_{Cr}$ is obtained for compound **4c** and its monometallic η^3-benzylic analog[1].

The ^{1}H-NMR spectra of compounds **4a**–**c** recorded at room temperature display very similar features. In all three cases the protons of the arene coordinated to the $Cr(CO)_3$ tripod resonate at ca. $\delta = 4.3-5.3$ as two doublets and one triplet each integrating one proton and at ca. $\delta = 6.3$ as a triplet integrating also one proton. A combination of two dimensional NMR experiments – e.g. COSY, NOESY and ^{1}H-^{13}C heteronuclear correlation – and the careful analysis of the multiplicities allowed the exact assignment of the proton resonances of the coordinated arene of compound **4a**. For instance, we assigned the signals at $\delta = 4.28$ (d, 1 H), 4.39 (d, 1 H), 5.23 (t, 1 H), and 6.32 (m, 2 H) to respectively H^6, H^3, H^4, and H^5; the latter overlaps with a signal of the pyridyl group. This wide outspreading of the ^{1}H resonances of the coordinated arene over a range of 2 ppm is reminiscent of that observed in tricarbonyl(η^5-cyclohexadienyl)chromium complexes[17]. It suggests that the arene coordinated to the chromium center in **4a** as well as in **4b** and **4c** has a much more pronounced η^5-cyclohexadienyl character than that suspected in reported cases of anionic (η^5-cyclohexadienyl)benzylidenetricarbonylchromium complexes[18]. Indeed, in known structurally characterized examples of tricarbonyl(η^5-cyclohexadienyl)chromium complexes the protons at the 2-, 3-, and 4-positions with respect to the sp^3 carbon atom resonate at $\delta = 2.4$, 3.7, and 6.0, respectively. The analogy made here lies on the assumption that at least H^3, H^4, and H^5 in complex **4a** are not submitted to some peculiar intramolecular magnetic anisotropy. Proton H^6 that resonates at a much lower frequency than H^4 may have underwent a slight shielding produced by the vicinal twisted pyridyl group. The significant geometrical distortions observed in the molecular structures of **4b** and **4c** support a "partial" η^5-bonding mode for the coordinated arene group.

Similarly to the observations made for complex **5**[1], the proton resonances of the phenyl group attached to the

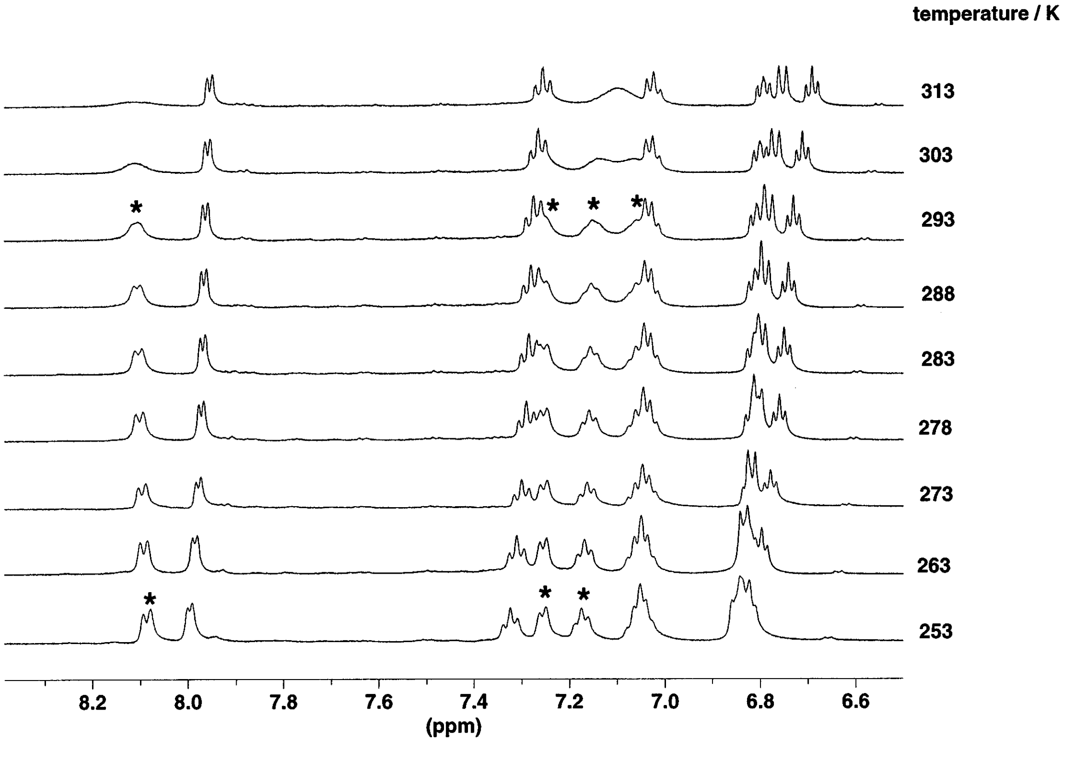
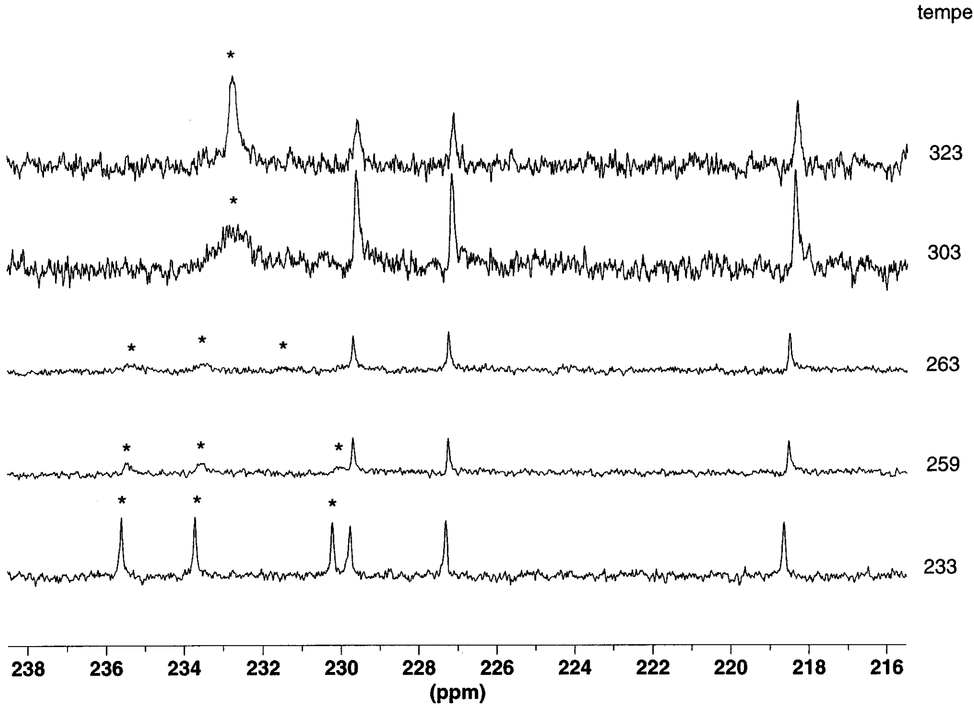


Figure 3. Temperature dependence of the ^{1}H NMR spectrum of **4a** in $CDCl_3$ in the so-called aromatic region. Asterisks designate the signals originating from the "slowly" rotating phenyl group

Figure 4. Temperature dependence of the ^{13}C-NMR resonances of the $Cr(CO)_3$ carbonyl ligands of **4a** in [D$_8$]THF. The asteriks indicate the signals that are involved in a dynamic process



pseudo-benzylic carbon of complexes **4a** and **4c** display a clear temperature dependence. At 293 K in [D$_6$]acetone, the signals of the phenyl group of **4a** appear as broad signals at δ = 7.10, 7.30, and 8.10 (Figure 3).

Cooling the sample to 253 K induces the decoalescence of these broad peaks, and leads to a consecutive sharpening of the signals and an increased resolution (Figure 3). Hence at that temperature, one may detect three distinct signals, a doublet at δ = 8.08 (*ortho* proton), a doublet at δ = 7.26 (*ortho* proton) and a triplet at δ = 7.18. The other signals produced by the phenyl fragment, two triplets for instance, remain mostly hidden behind several intense multiplets attributed to the protons of the pyridyl group approximately at δ = 7.05 and 6.85. Due to the large separation in frequency between two exchanging protons the coalescence temperature of the two-site-exchange systems composed of two related doublets and two related triplets is not readily detectable. Heating the sample even up to 313 K did not provide a clear localization of the fast exchange signals (Figure 3).

Complex **4b** behaves in a slightly different way since at room temperature the signals of the phenyl group reflect, in the NMR time scale, a pattern consistent with a slow two site exchange[19]. Among the seven signals that can be readily observed at 298 K in deuterated acetone in the range from 6.7 to 8.5 ppm two resolved signals produced by the phenyl group are clearly separated from the rest of the spectrum and are detected at δ = 7.88 (d, 1 H) and 7.21 (t, 1 H). The integration of the overall area of the spectrum in the δ = 6.7–8.5 range confirms the presence of eight aromatic protons.

The steric bulk encountered in both molecular structures of **4b** and **4c** implies an underlying fluxional behavior of the $Cr(CO)_3$ rotor. Consequently, the ^{13}C-NMR spectra of **4a**–**c** performed at 298 K show a broad signal at about δ = 233 accounting for the rotating $Cr(CO)_3$ moiety and three sharp signals at δ = 229, 228, and 218 that can be assigned undoubtedly to the carbonyl resonances of the chelated static $Mn(CO)_3$ fragment. Variable-temperature NMR experiments were carried out with [D$_8$]THF solutions of compound **4a** (Figure 4).

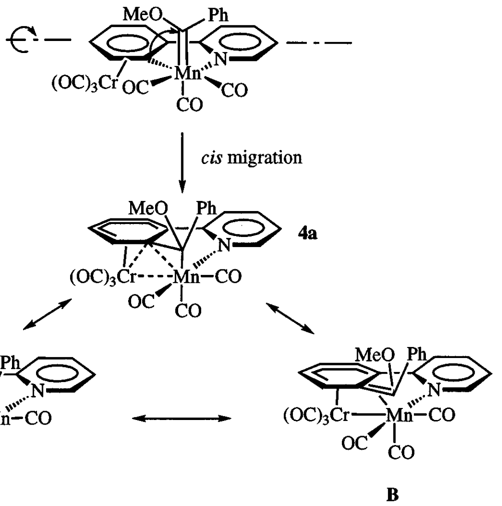
At 233 K, complete decoalescence already took place and the resulting spectrum reveals, apart from the resonances of the manganese-coordinated carbonyl ligands at δ = 229.7, 227.3, and 218.6, three other low field sharp singlets at δ = 235.6, 233.7, and 230.2 consistent with a $Cr(CO)_3$ moiety which rotates relatively slowly in an asymmetric environment[20] (Figure 4). Further experiments are underway with ^{13}CO enriched samples that should yield the main thermodynamical factors related to the hindered rotation of $Cr(CO)_3$.

4. Discussion

The facile cyclomanganation of (η^6-arene)tricarbonylchromium complexes bearing nitrogen based chelating ligands has offered us an interesting starting point for the further exploration of possible applications of chelated $Mn(CO)_4$ complexes. In a recent paper we addressed the reactivity of 2-phenylpyridine–$Mn(CO)_4$ complexes toward organolithium reagents. This study indicated that the reactivity of these metallacycles, that may also be formulated as *cis*-$L_2Mn(CO)_4$, toward organolithium reagents, RLi, corresponds to that of the intensively studied $M(CO)_6$ complexes (M = Cr, Mo, W). The main difference between these two systems is the fact that addition of RLi in the reaction involving $Mn(CO)_4$ chelates takes place exclusively at an axial carbonyl ligand. The trapping of the anionic acyl intermediates and subsequent NMR analyses never provided evidence for the formation of more than one anionic isomer. A study carried out with an analogous $Re(CO)_4$ complex allowed us to isolate and characterize an acetylrhenate complex that bears the CH_3CO- fragment at an axial position, *trans* to a CO ligand[21]. The addition of PhLi to the bimetallic starting materials selectively takes place at one carbonyl ligand of the $Mn(CO)_4$ moiety. Given the steric bulk of the $Cr(CO)_3$ tripod the *exo* axial CO ligand of the $Mn(CO)_4$ fragment is preferred to undergo a facile nucleophilic addition leading to a benzoylmanganate intermediate. The resulting anionic intermediate is greatly stabilized by a large delocalisation of the negative charge throughout the molecule. Three limit formulae may account reasonably for the charge redistribution as it is shown in Scheme 1 for **3a−c**.

We proposed in our early studies[1] that the treatment of the anionic acyl manganates by a hard alkylating agent such as MeOTf may yield a transient electrophilic alkoxyalkylidene complex[22]. A similar proposal can be made here (Scheme 3).

Scheme 3



We speculate that such a species may undergo a *cis*-migration of the $Cr(CO)_3$-coordinated phenyl group to the manganese bound alkylidene carbon atom resulting in a *syn*-arrangement of the two tricarbonylmetal fragments (Scheme 3). We already reported that in the process leading to **5** the manganese atom must coordinate in part to the vicinal aromatic ligand to meet the 18 valence electrons requirement. In the new compounds presented here, this electronic requirement seems to be met through a dative or a donor-acceptor interaction with the saturated chromium atom. The results of the low temperature ^{13}C-NMR experiments done with **4a** indicate that $Cr(CO)_3$ still behaves as a rotor and that the Mn−Cr interaction must be quite weak. Indeed, each complete rotation of the $Cr(CO)_3$ tripod must correspond to at least three single metal-metal bond disruptions.

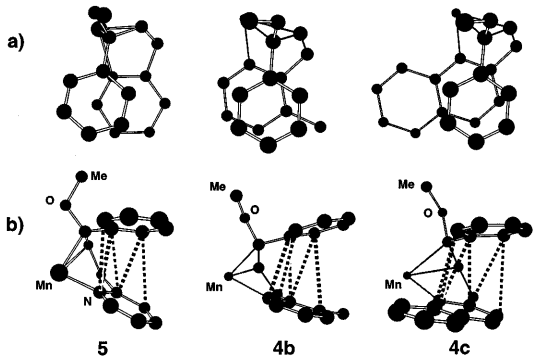
In a very recent study Ceccon and co-workers have reported the preparation and the structural chacterization of *syn*-facial heterobimetallic complexes *syn*-[$Cr(CO)_3$-μ,η:η-indenyl−ML] (M = Rh[23], L = COD, $(CO)_2$, NBD; M = Ir[24], L = COD). In most of these cases a weak non-covalent chromium-metal interaction, Cr−M, is invoked to explain the stability of the complexes. Similar to our two examples the $Cr(CO)_3$ tripod is shifted away from its common η^6 bonding mode to rather pronounced η^5 and η^4 hapticities. In general, a relevant distortion of the indenyl ligand accompanies these peculiar metal−metal interactions. Although a hindered rotation of the $Cr(CO)_3$ tripod is very likely it is not mentioned. The latter Cr−M interactions are even suspected by the authors to thermodynamically stabilize the *syn*-facial isomers whereas the analogous *trans* bimetallic complexes offer a much different reactivity. Depending on the steric bulk and the electronic nature of the ligand coordinating either Rh or Ir in these cases the Cr−M (M = Rh, Ir) distances vary from typically 3.07 Å (M = Ir, L = COD) to 3.3 Å (M = Rh, L = NBD). Similar significant differences for the Cr−Mn interatomic distance are not observed for **4b** and **4c**. However, we definitively may assess that metal-metal electronic interactions play a role. Ceccon's *syn*-facial heterobimetallic complexes are synthesized by a ligand exchange reaction between $(CH_3CN)_3Cr(CO)_3$ and a η^3 coordinated indenyl iridium or rhodium complex in THF. A similar synthetic pathway applied to complex **5** did not yield compound **4a** even when the ligand-exchange reaction was done at 80°C in DME.

The main common trend that exists between the three crystallographically characterized complexes **5**, **4b**, and **4c** is the overlaying of the phenyl, pyridyl, and quinolinyl groups. This is well illustrated by the overlap diagrams grouped in the upper part of Figure 5 which outlines that in the more sterically hindered complexes **4b-c** the overlay of the phenyl and the N-heterocyclic ring is larger. In the lower part of Figure 5 the dashed lines indicate those interatomic distances between the two stacked rings that are inferior or equal to 3.5 ±0.1 Å, a value generally ascertained for optimal stabilizing π-stacking interactions in polyaromatic molecules or in crystal lattices of aromatic compounds[25]. The values of the interplanar angles between the phenyl group and the vicinal N-heterocycle in **4b−c** are 34.9° and 25.0°.

It is well established that the nature of the inter- or intramolecular π-stacking interactions is determined by five different categories of effects: the Van der Waals and electrostatic interactions, the induction energy, the charge-transfer and the desolvation of each molecule/fragment before interaction. Each of these effects depends directly on the nature of the aromatics that are involved and contributes in various orders of magnitude in a given interaction[25b].

It is noteworthy that the process which leads to the *syn*-facial bimetallic complexes afford solely the eclipsed stereo-

Figure 5. π-Stacking of phenyl and N-heterocyclic groups in compounds **5**, **4b**, **4c**. The adjacent aromatic ring has been omitted for clarity. a) top views and overlap diagrams. b) side views of the stakking interactions: the dashed bonds indicate interatomic distances that are shorter than 3.5 ± 0.1 Å



isomers in which the phenyl group eclipses the N-heterocycle as in **5** and **4b−c**. The other possible staggered product, which was not detected, would place the methoxy group above the heterocycle. At this point one might propose that the apparent selectivity of the reaction leading to **5** and **4a−c** from the alkylation of the corresponding acylmanganate species stems from a thermodynamic control that favors the eclipsed isomer through an intramolecular π-π interaction. Further experiments are underway to verify this hypothesis.

In conclusion, the reaction of cyclomanganated (η^6-arene)tricarbonylchromium complexes with PhLi and subsequent treatment with MeOTf yields new *syn*-facial heterobimetallic cyclohexadienylbenzylidene complexes in which the manganese atom interacts directly with the metal centre of the $Cr(CO)_3$ tripod. Although the exact nature of this interaction is not yet established it ressembles a donor-acceptor metal-metal bond. In this paper we have described a new methodology for the synthesis of *syn*-facial organobimetallic complexes and we have found a novel application of cyclometallated (η^6-arene)tricarbonylchromium complexes. We intend to further investigate the mechanistic aspects of their formation as well as the theoretical underlying issues.

We gratefully acknowledge the financial support provided by the *Centre National de la Recherche Scientifique*, the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie*. We thank Ms. *Ulrike Weynand* (Kékulé Institute of Organic Chemistry and Biochemistry − University of Bonn) for performing the low temperature NMR experiments and Dr. *Kamel Harrata* for HR-MS measurements.

Experimental Section

General: All reactions were carried out under a dry nitrogen atmosphere. (η^6-Arene)tricarbonylchromium complexes were prepared using the procedure of Pauson and co-workers[26]. Benzylpentacarbonylmanganese[27] and complexes **1a**, **2a**, **1b**, and **2b** were prepared by following literature procedures[4b]. The reaction products were separated by flash chromatography on silica gel (Merck, 60 µm) under a dry nitrogen atmosphere. High-resolution mass spectra were recorded at the Mass Spectrometry Service of the Iowa State University, U.S.A. Elemental analyses were done in presence of a combustion aid (V_2O_5) at the "Service de Microanalyse de l'Institut de Chimie", Strasbourg, France. Subambient temperature NMR experiments were done at the Analytical Center of the Chemical Institutes, University of Bonn, Germany. − IR: Perkin-Elmer FT. − NMR: Bruker AC 300, DRX 500 (300 MHz and 500 MHz for ^{1}H, 75 MHz and 125 MHz for ^{13}C). ^{13}C NMR spectra reported herein were all done with proton decoupling. The atom numbering used in the systematic nomenclature of the undermentioned compounds does not follow necessarily the one used for convenience throughout the results and discussion parts.

2-[(η^6-Phenyl)tricarbonylchromium]quinoline (**1c**): In a mixture of 8 ml of THF and 80 ml of di-*n*-butyl ether were dissolved 2-phenylquinoline (0.94 g, 4.58 mmol) and hexacarbonylchromium (1.51 g, 6.87 mmol). The resulting mixture was brought to refluxed for 51 hours under an atmosphere of nitrogen until signs of decomposition appeared in the reaction medium. The solution was cooled to room temperature and filtred over Celite, and both the solvents and the unreacted $Cr(CO)_6$ were removed under reduced pressure. The crude oily residue was then redissolved in dry diethyl ether and the solution mixed with silica gel. The solvent was removed under reduced pressure, and the resulting coated silica gel was loaded on the top of a silica gel column packed in dry and degassed hexane. The unreacted arene ligand was eluted first with CH_2Cl_2/hexane (4:6). The 2-[(η^6-phenyl)tricarbonylchromium]quinoline complex, **1c**, was then eluted with CH_2Cl_2/hexane (8:2). The solvents were evaporated under reduced pressure. Recrystallization from dry hexane gave 1.17 g of **1c** (75%) as orange crystals, m.p. 130°C. − IR (CH_2Cl_2): $\tilde{\nu}$ = 1971 (CO), 1897 cm^{-1} (CO). − ^{1}H NMR ($CDCl_3$): δ = 5.52 (m, 3 H, H_{ArCr}), 6.37 (d, J = 5.4 Hz, 2 H, H_{ArCr}), 7.56 (t, J = 7.1 Hz, 1 H, H_{Ar}), 7.65 (d, J = 8.8 Hz, 1 H, H_{Ar}), 7.74 (t, J = 7.6 Hz, 1 H, H_{Ar}), 7.83 (d, J = 8.3 Hz, 1 H, H_{Ar}), 8.10 (d, J = 8.5 Hz, 1 H, H_{Ar}), 8.22 (d, J = 8.3 Hz, 1 H, H_{Ar}). − ^{13}C NMR ($CDCl_3$): δ = 91.8 (C_{ArCr}), 92.6 (C_{ArCr}), 92.7 (C_{ArCr}), 105.2 (C_{ArCr}), 117.6, 127.0, 127.5, 127.7, 129.6, 130.1, 137.0, 147.7, 153.4, 232.4 (Cr-*CO*). − $C_{18}H_{11}CrNO_3$ (341.3): calcd. C 63.29, H 3.22, N 4.10; found C 63.51, H 3.16, N 4.10.

[2-[(η^6-Phenyl-κ$C^{1'}$)tricarbonylchromium](quinoline-κN)]tetracarbonylmanganese (**2c**): A solid mixture of complex **1c** (275 mg, 0.806 mmol) and $PhCH_2-Mn(CO)_5$ (253 mg, 0.887 mmol) was dissolved in a minimum volume (10 ml) of dry heptane and gently stirred at the boiling temperature of the solvent. After 4 hours, the reaction mixture was cooled to room temperature, and evaporated under reduced pressure. The residue was redissolved in CH_2Cl_2 and mixed with silica gel. The solvent was removed under reduced pressure, and the resulting coated silica gel loaded on the top of a silica gel column packed with dry and degassed hexane. [2-{(η^6-Phenyl-κ$C^{1'}$)tricarbonylchromium}(quinoline-κ*N*)]-tetracarbonylmanganese, **2c**, was eluted with CH_2Cl_2/hexane (4:6). The solvents were then evaporated under reduced pressure and recrystallization of the resulting solid from dry hexane gave 267 mg of **2c** (65%), red crystals, m.p. 190°C (decomposition). − IR (CH_2Cl_2): $\tilde{\nu}$ = 2086, 2007, 1985, 1955, 1944, 1884 cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 5.47 (t, J = 6.2 Hz, 1 H, H_{ArCr}), 5.58 (t, J = 6.4 Hz, 1 H, H_{ArCr}), 5.92 (d, J = 6.1 Hz, 1 H, H_{ArCr}), 6.24 (d, J = 6.3 Hz, 1 H, H_{ArCr}), 7.63−7.71 (m, 2 H, H_{Ar}), 7.85 (m, 2 H, H_{Ar}), 8.32 (d, J = 8.5 Hz, 1 H, H_{Ar}), 8.62 (d, J = 9.3 Hz, 1 H, H_{Ar}). − ^{13}C NMR ($CDCl_3$): δ = 90.05 (C_{ArCr}), 92.72 (C_{ArCr}), 92.86 (C_{ArCr}), 104.69 (C_{ArCr}), 112.83 (C_{ArCr}), 116.93 (C_{ArCr}), 127.5, 127.9, 128.4, 129.1, 131.7 139.7 140.1, 149.8, 167.3 210.2 (Mn-*CO*), 211.1 (Mn-*CO*), 212.5 (Mn-*CO*), 220.1 (s, Mn-*CO*), 234.5 (s, Cr-*CO*). − $C_{22}H_{10}CrMnNO_7$ (507.3): calcd. C 52.09, H 1.99, N 2.76; found C 52.23, H 1.99, N 2.72.

General Procedure for the Synthesis of Complexes **4a**−**c**: Bimetallic complexes **2a-c** were separately dissolved in DME and the solution was cooled to −50°C. A solution of phenyllithium (1.8 M in cyclohexane/ether, Aldrich Chemicals) was then added and the temperature of the reaction mixture was allowed to reach −20°C. After 10 min at −20°C, the reaction mixture was cooled to −40°C. Methyltrifluoromethanesulfonate was added and the reaction mixture slowly warmed to room temperature. The solvent was removed in vaccuo and the residue dissolved in CH_2Cl_2 and mixed with silica gel, the solvent removed under reduced pressure. The resulting coated silica gel was loaded on the top of a silica gel column that was packed in dry and degassed hexane and eluted with mixtures of CH_2Cl_2 and hexane.

2-{2′,3′,4′,5′,6′-η^5-[1′(α-methoxybenzylidene-κC^α)cyclohexadienyl-κ$C^{1'}$]tricarbonylchromium}(pyridine-κN)tricarbonylmanganese(Cr-Mn) (**4a**): Complex **2a** (413 mg, 0.90 mmol), PhLi (0.55 ml, 0.99 mmol), MeOTf (0.14 ml, 1.26 mmol). Chromatography on SiO_2 with CH_2Cl_2/hexane (7:3). Evaporation of the solvents gave 331 mg of **4a** (67%), as a red amorphous powder, m.p. 200−210°C (decomposition). − IR (CH_2Cl_2): $\tilde{\nu}$ = 2010.0, 1962.1, 1929.1, 1885.8 cm^{-1}. − ^1H NMR (C_3D_6O): δ = 3.29 (s, 3 H, OMe), 4.47 (d, J = 7.5 Hz, 1 H, H_{ArCr}), 4.82 (d, J = 6.3 Hz, 1 H, H_{ArCr}), 5.56−5.61 (m, 1 H, H_{ArCr}), 6.68−6.80 (m, 3 H), 7.01 (d, J = 7.0 Hz, 1 H), 7.09 (broad, 2 H, H_{Ar}), 7.25 (t, J = 7.9 Hz, 2 H), 7.93 (d, J = 5.5 Hz, 1 H), 8.08 (broad, 1 H). − ^1H NMR (CD_2Cl_2): δ = 3.33 (s, 3 H, OMe), 4.28 (d, 1 H, H_{ArCr}), 4.39 (d, 1 H, H_{ArCr}), 5.23 (t, 1 H, H_{ArCr}), 6.32 (m, 2 H), 6.57 (m, 1 H), 6.97−7.04 (m, 2 H, H_{Ar}), 7.10 (broad), 7.20 (broad), 7.84 (d, 1 H, H_{Ar}), 8.10 (broad). − ^{13}C NMR (CD_2Cl_2): δ = 55.2 (Me), 80.3 (C_{ArCr}), 82.9 (C_{ArCr}), 85.9 (C_{ArCr}), 88.7 (1 C, C_{ArCr}), 91.5 (C_{ArCr}), 91.6 (C_{ArCr}), 96.6, 118.8, 123.4, 127.0, 128.1, 131.3 (broad, 1 C), 134.5 (broad, 1 C), 138.0, 142.5, 152.9 , 159.0 , 220.3 (1 C, Mn-*CO*), 229.3 (1 C, Mn-*CO*), 231.0 (1 C, Mn-*CO*), 234.1 (broad, 3 C, Cr-*CO*). − $C_{25}H_{16}CrMnNO_7$ (549.34): calcd. C 54.66, H 2.94, N 2.55; found C 54.82, H 2.92, N 2.51.

[2-{2′,3′,4′,5′,6′-η^5-[1′(α-methoxy-benzylidene-κC^α)cyclohexadienyl-κC1′]tricarbonylchromium},3-methylpyridine-κN]tricarbonylmanganese(Cr−Mn) (**4b**): Complex **2b** (387 mg, 0.82 mmol) in 10 ml of DME at −50°C. Addition of PhLi (0.50 ml, 0.90 mmol), MeOTf (0.12 ml, 1.08 mmol). Chromatography on SiO_2 with CH_2Cl_2/hexane (7:3). Evaporation of the solvents gave 323 mg of **4b** (70%) as red crystals, m.p. 210°C (decomposition). − IR (CH_2Cl_2): $\tilde{\nu}$ = 2009, 1960, 1927, 1884 cm^{-1}. − MS (EI): *m/z* = 562.9 $[M]^+$, 507.0 $[M - 2\ CO]^+$, 479.1 $[M - 3\ CO]^+$, 395.1 $[M - 4\ CO - Mn]^+$, 340.1, 310.1, 257.2. − ^1H NMR (C_3D_6O): δ = 1.86 (s, 3 H, Me), 3.33 (s, 3 H, OMe), 4.43 (dd, ^3J = 7.4 Hz ^4J = 1.1 Hz, 1 H, H_{ArCr}), 4.74 (dd, ^3J = 6.2 Hz ^4J = 1.2 Hz, 1 H, H_{ArCr}), 5.49−5.54 (m, 1 H, H_{ArCr}), 6.60−6.70 (m, 2 H), 6.98−7.05 (m, 3 H), 7.21 (broad, 1 H, H_{Ar}), 7.37 (broad, 1 H), 7.85 (broad, 1 H), 7.88 (d, J = 5.5 Hz, 1 H). − ^{13}C NMR (CD_2Cl_2): δ = 21.2 (Me), 56.7 (OMe), 82.0 (C_{ArCr}), 85.5 (C_{ArCr}), 87.0 (C_{ArCr}), 90.9 (C_{ArCr}), 91.2 (C_{ArCr}), 93.0 (C_{ArCr}), 100.4 124.3, 128.8, 129.6, 130.0 132.5, 133.8, 135.0, 141.9, 144.3, 152.2, 157.7, 222.0 (1 C, Mn-*CO*), 231.4 (1 C, Mn-*CO*), 232.6 (1 C, Mn-*CO*), 236.5 (broad, 3 C, Cr-*CO*). − $C_{26}H_{18}CrMnNO_7$ (563.36): calcd. C 55.43, H 3.22, N 2.49; found C 56.71, H 2.83, N 2.45.

[2-{2′,3′,4′,5′,6′-η^5-[1′(α-methoxybenzylidene-κC^α)cyclohexadienyl-κ$C^{1'}$]tricarbonylchromium}quinoline-κN]tricarbonylmanganese(Cr-Mn) (**4c**): Complex **2c** (226 mg, 0.44 mmol), PhLi (0.27 ml, 0.49 mmol), MeOTf (0.10 ml, 0.90 mmol). Chromatography on SiO_2 with CH_2Cl_2/hexane (5:5). Evaporation of the solvents gave 119 mg of **4c** (45%) as red crystals, m.p. 190°C (decomposition). − MS (EI): *m/z* 599.0 $[M]^+$, 542.9 $[M - 2\ CO]^+$, 433.1 $[M - 3\ CO - Cr]^+$, 372.9, 344.9, 293.2. − IR (CH_2Cl_2): $\tilde{\nu}$ = 2009, 1960, 1927, 1885 cm^{-1}. − ^1H NMR (CD_2Cl_2): δ = 3.34 (s, 3 H, OMe), 4.25 (dd, ^3J = 6.1 Hz ^4J = 1.4 Hz, 1 H, H_{ArCr}), 4.37 (dd, ^3J = 7.5 Hz ^4J = 0.9 Hz, 1 H, H_{ArCr}), 5.23−5.26 (m, 1 H, H_{ArCr}), 6.36 (d, J = 8.5 Hz, 1 H, H_{Ar}), 6.40 (td, ^3J = 6.1 Hz ^4J = 0.9 Hz, 1 H, H_{ArCr}), 6.57 (broad, 1 H, H_{Ar}), 6.85−6.87 (m, 1 H, H_{Ar}), 7.06 (broad, 1 H, H_{Ar}), 7.32 (broad, 1 H, H_{Ar}), 7.43 (broad, 1 H, H_{Ar}), 7.48−7.51 (m, 3 H), 7.87−7.91 (m, 1 H), 8.46−8.48 (m, 1 H). − ^{13}C NMR (CD_2Cl_2): δ = 55.4 (OMe), 81.2, 81.9, 85.1, 88.3, 90.9, 91.7, 96.9, 116.7, 127.4−129.0 (m, 8 C), 132.6, 134.2, 139.6, 142.1, 147.8, 160.6, 221.0 (1 C, Mn-*CO*), 231.8 (2 C, Mn-*CO*), 234.9 (broad, 3 C, Cr-*CO*). − $C_{29}H_{18}CrMnNO_7$ (599.40): calcd. C 58.11, H 3.03, N 2.34; found C 58.31, H 2.92, N 2.28. − High-resolution MS (EI) for $C_{29}H_{18}CrMnNO_7$: calcd. 598.986921; found (deviation) 598.98786 (1.4 ppm).

Table 3. Details of data collection and refinement for compounds **4b** and **4c**

Compound	**4b**	**4c**
Formula	$C_{26}H_{18}NO_7CrMn\cdot CH_2Cl_2$	$C_{29}H_{18}NO_7CrMn$
M_r	648.3	599.4
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$ (No.14)	P-1 (No.2)
a [Å]	9.5000(2)	8.8643(2)
b [Å]	13.6195(2)	9.8096(2)
c [Å]	20.9739(2)	15.6363(3)
α [deg]	90	76.387(1)
β [deg]	101.175(1)	74.656(1)
γ [deg]	90	72.519(1)
V [Å^3]	2662.26(7)	1232.55(4)
Z	4	2
crystal size [mm^3]	0.40 × 0.20 × 0.15	0.35 × 0.30 × 0.10
ρ_{calc} [g·cm^{-3}]	1.62	1.62
μ [mm^{-1}]	1.131	1.005
F(000)	1312	608
Diffractometer	Nonius Kappa-CCD	Nonius Kappa-CCD
Radiation	Mo-K	Mo-$K\alpha$
λ [Å]	0.71013	0.71013
T [K]	123(2)	123(2)
max 2θ, [deg]	56.6	56.6
index range	$-12 < h < 12$ $-17 < k < 17$ $-23 < l < 23$	$-11 < h < 11$ $-13 < k < 12$ $-20 < l < 20$
No. of data	32570	19147
No. of unique data	5498	4557
R_{int}	0.024	0.019
No. of data with $I>2\sigma(I)$	4805	4193
Parameters/Restraints	353/16	353/0
$R(F)$ for $I>2\sigma(I)$	0.032	0.026
$wR2(F^2)$ for all data	0.090	0.074
goodness of fit on F^2	1.09	1.06
largest diff. peak and hole [e·Å^{-3}]	0.816/−0.840	0.271/−0.456

Isolation and Spectroscopic Characterization of Complex **3a**-PPN: A THF solution of complex **2a** was combined with a solution of phenyllithium in hexane at −50°C. The resulting dark orange solution was warmed to −20°C after 40 min and evaporated. The resulting oily residue was triturated with hexane. The supernatant was removed and the air and temperature sensitive solid residue dried under vacuum and added with PPN^+Cl^-. The solid mixture was dissolved in a minimum amount of dichloromethane. A few drops of diethyl ether were added to the solution in order to induce the precipitation of LiCl and the mixture filtered through celite. The filtrate was then evaporated under vacuum and the oily redish residue washed twice with diethyl ether to induce crystallization of **3a**-PPN. Elemental analysis of the latter did not provide satisfactory values due to fast decomposition during the sample preparation process. − IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 1972 (m), 1930 (m), 1844 (vs), 1558 (w) cm^{-1}. − ^{1}H NMR (CD$_2$Cl$_2$): 5.23 (t,1 H), 5.36 (t, 1 H), 5.95 (d, 1 H), 6.27 (d, 1 H), 6.95−7.19 (m, 6 H), 7.16−7.71 (m, 32 H), 8.90 (d, 1 H). − ^{13}C NMR (CD$_2$Cl$_2$): 90.8 (C$_{ArCr}$), 91.2 (C$_{ArCr}$), 93.3 (C$_{ArCr}$), 105.8, 118.6, 121.2, 123.7 , 126.3 , 126.9, 127.1, 127.7, 129.8 (m, PPN$^+$), 132.4 (m, PPN$^+$), 134.0 (s, PPN$^+$), 135.3, 153.0, 154.8, 164.3, 164.8, 168.8, 219.7 (Mn-*CO*), 222.9 (Mn-*CO*), 231.1 (Mn-*CO*), 237.5 (Cr-*CO*), 289.5 (Ph*CO*-Mn).

Procedure for the Structure Determination of **4b** *and* **4c**: The molecular structures of **4b** and **4c** were solved by direct methods (SHELXTL-Plus)[28]. The non hydrogen atoms were refined anisotropically on F^2 (SHELXL-93)[29]. Hydrogen atoms were refined isotropically using a riding model. An empirical absorption correction was applied (**4b**: $T_{\mathrm{max./min.}}$ = 0.4956/0.4442, **4c**: $T_{\mathrm{max./min.}}$ = 0.7996/0.6693). In **4b** the solvent is disordered. Further details are given in Table I. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101430. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code +44 (1223) 336−033; e-mail: deposit@ccdc.cam.ac.uk].

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[6] List of the abbreviations used throughout this article: DME, 1,2-dimethoxyethane; THF, tetrahydrofuran; MeOTf, methyltriflate or methyltrifluoromethanesulfonate; PPN, bis(triphenylphosphoranylidene)ammonium; PhLi, phenyllithium; MeLi, methyllithium; COD, cyclooctadiene; NBD, norbornadiene.

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