

JOM 23451

Comparative multinuclear magnetic resonance spectroscopic study of transition metal (Cr, W and Mn) mesitylene tricarbonyls and transition metal (Ru and Co) carbonyl clusters

E. Kolehmainen ^a, K. Laihia ^a, M.I. Rybinskaya ^b, V.S. Kaganovich ^b and Z.A. Kerzina ^b

^a Department of Chemistry, University of Jyväskylä, PO Box 35, SF-40351 Jyväskylä (Finland)

^b A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov Str. 28, 117813 Moscow (Russia)

(Received November 11, 1992)

Abstract

Three mononuclear 1,3,5-trimethylbenzene (mesitylene) carbonyl transition metal complexes, mesitylene tricarbonyl chromium, $(\text{CH}_3)_3\text{C}_6\text{H}_3\text{Cr}(\text{CO})_3$ (**1**), mesitylene tricarbonyl tungsten, $(\text{CH}_3)_3\text{C}_6\text{H}_3\text{W}(\text{CO})_3$ (**2**), mesitylene tricarbonyl manganese tetra-fluoroborate, $[(\text{CH}_3)_3\text{C}_6\text{H}_3\text{Mn}(\text{CO})_3]\text{BF}_4$ (**3**); and three clusters, mesitylene nonacarbonyl tetracobalt, $(\text{CH}_3)_3\text{C}_6\text{H}_3\text{Co}_4(\text{CO})_9$ (**4**), mesitylene carbido tetradecacarbonyl hexaruthenium, $(\text{CH}_3)_3\text{C}_6\text{H}_3\text{Ru}_6\text{C}(\text{CO})_{14}$ (**5**) and carbido heptadecacarbonyl hexaruthenium, $\text{Ru}_6\text{C}(\text{CO})_{17}$ (**6**), have been studied by means of ¹H, ¹³C and natural abundance ¹⁷O NMR spectroscopy. Generally, the ¹H and ¹³C NMR chemical shifts of the aromatic protons and carbons in the compounds studied show clearly shielded values when compared with those of uncomplexed mesitylene. The ¹³C NMR chemical shifts of the carbonyl groups show an inverse relation with the corresponding ¹⁷O chemical shifts in agreement with the effect of π -backbonding. ¹J(C, H) spin-spin coupling constants of aromatic carbons in mesitylene moiety of chromium and tungsten complexes show clearly increased values when compared with uncomplexed mesitylene. This can be explained by an increased s-character in the C–H bond induced by the σ -effect of the bound metal. Of the NMR methods studied, ¹⁷O NMR was shown to have very promising properties owing to the exceptionally high sensitivity and small line width of NMR signals.

1. Introduction

¹³C NMR data on organometallic carbonyl compounds have been collated by Mann and Taylor [1], but there has been little success with theoretical treatments of ¹³C NMR chemical shifts of organometallic compounds (ref. 1, p. 9), so additional studies are necessary.

Regarding the ¹H NMR chemical shifts of the transition metal π -complexes, the clear increases in the shieldings of aromatic protons have been explained qualitatively in terms of influence of asymmetrical charge distribution of valence orbitals of the transition metal [2]. The resulting magnetic moment deshields the metal nucleus itself at the same time [2].

In spite of the availability of ¹³C NMR data on metal carbonyls [1], only a few papers have dealt with ¹³C and ¹⁷O NMR spectroscopy of arene transition

metal carbonyls such as toluene or xylene tricarbonyl chromium, tungsten and manganese complexes [3,4]. ¹⁷O NMR spectroscopy, however, has been shown to have great promise for studies of Mn, Fe and Co carbonyls owing to favourable NMR linewidths over a wide temperature range [5].

We describe a multinuclear magnetic resonance spectroscopic study of mesitylene carbonyl π -complexes of five different metals *viz.* mesitylene tricarbonyl chromium, $(\text{CH}_3)_3\text{C}_6\text{H}_3\text{Cr}(\text{CO})_3$ (**1**), mesitylene tricarbonyl tungsten, $(\text{CH}_3)_3\text{C}_6\text{H}_3\text{W}(\text{CO})_3$ (**2**), mesitylene tricarbonyl manganese tetrafluoroborate, $[(\text{CH}_3)_3\text{C}_6\text{H}_3\text{Mn}(\text{CO})_3]\text{BF}_4$ (**3**), and three clusters, mesitylene nonacarbonyl tetracobalt, $(\text{CH}_3)_3\text{C}_6\text{H}_3\text{Co}_4(\text{CO})_9$ (**4**), mesitylene carbido tetradecacarbonyl hexaruthenium, $(\text{CH}_3)_3\text{C}_6\text{H}_3\text{Ru}_6\text{C}(\text{CO})_{14}$ (**5**), and carbido heptadecacarbonyl hexaruthenium, $\text{Ru}_6\text{C}(\text{CO})_{17}$ (**6**). This was carried out in order to deepen our knowledge of their ¹⁷O NMR spectroscopic properties and to compare the data obtained for these substances by multinuclear magnetic resonance methods.

Correspondence to: Dr. E. Kolehmainen.

Considering this series of compounds, the elements Cr and W are typical representatives of the Group 6 transition metals and Mn is a representative of Group 7. The cationic moiety in mesitylene tricarbonyl manganese can be used in estimating the influence of the charge on the observed NMR parameters. Ru and Co are representative transition metals of Groups 8 and 9, respectively. Further, three of the clusters provide opportunities for clarifying the differences between mono- and polynuclear transition metal derivatives.

Multinuclear magnetic resonance spectroscopy is an especially attractive method for these studies, because ^1H , ^{13}C and ^{17}O nuclei can probe the transition metal at different distances.

2. Experimental section

2.1. Syntheses

Compounds **1–6** were synthesized by the following procedures:

1 (mesitylene tricarbonyl chromium, $(\text{CH}_3)_3\text{C}_6\text{H}_3\text{-Cr}(\text{CO})_3$ [6]. A mixture of $\text{Cr}(\text{CO})_6$ (0.50 g; 2.3 mmol) and 3 ml of mesitylene in 50 ml of diglyme and 10 ml of heptane was refluxed for 6 h (up to the end of the process of carbonyl sublimation). After cooling, the solvent was evaporated under reduced pressure. The residue was chromatographed on an Al_2O_3 column using benzene/petroleum ether mixture (1:1, v/v) as an eluent. The yellow band was collected giving the product (yield: 60%).

2 (mesitylene tricarbonyl tungsten, $(\text{CH}_3)_3\text{C}_6\text{H}_3\text{-W}(\text{CO})_3$ [7]. The procedure was the same as for **1**. 1.0 g (2.8 mmol) of $\text{W}(\text{CO})_6$ gave **2** (yield: 35%).

3 (mesitylene tricarbonyl manganese tetrafluoroborate, $[(\text{CH}_3)_3\text{C}_6\text{H}_3\text{Mn}(\text{CO})_3]\text{BF}_4$) [8]. A mixture of $\text{ClMn}(\text{CO})_5$ (0.23 g; 1.0 mmol) and 0.5 ml of mesitylene in 5 ml of CF_3COOH was refluxed for 2 h (until the colour became yellow). After cooling, 0.3 ml of 48% aqueous HBF_4 was added. The solvent was evaporated under reduced pressure. The residue was washed with ether and reprecipitated from a mixture of ether and CH_3NO_2 . The yield was 75%.

4 (mesitylene nonacarbonyl tetracobalt, $(\text{CH}_3)_3\text{C}_6\text{H}_3\text{Co}_4(\text{CO})_9$) [4]. A mixture of $\text{Co}_2(\text{CO})_8$ (0.34 g; 1.0 mmol) and 3 ml of mesitylene in 70 ml of hexane was refluxed for 22 h. After cooling, the solution was chromatographed on a silica gel column using a mixture of benzene/petroleum ether (1:5, v/v) as an eluent. After separation of the first brown band containing an excess of ligand and some nonreacted cobalt carbonyl, a dark-green band was collected. After evaporating the solvent under reduced pressure, the yield of **4** was 55%.

5 (mesitylene carbido tetradecacarbonyl hexaruthenium $(\text{CH}_3)_3\text{C}_6\text{H}_3\text{Ru}_6\text{C}(\text{CO})_{14}$ and **6** (carbido heptadecacarbonyl hexaruthenium, $\text{Ru}_6\text{C}(\text{CO})_{17}$) [9]. A mixture of $\text{Ru}_3(\text{CO})_{12}$ (0.50 g; 0.78 mmol) and 3 ml of mesitylene in 60 ml of octane was refluxed for 14 h. After cooling, the reaction mixture was chromatographed on a SiO_2 column. From the first, orange-red band, the product $\text{Ru}_6(\text{CO})_{17}$ (**6**) was obtained with a yield of 45%. From the following, dark purple-brown band, the arene complex **5** was isolated with a yield of 7%.

2.2. NMR spectroscopy

^1H , ^{13}C and ^{17}O NMR spectra were recorded on a Jeol GSX 270 MHz spectrometer working at 270.17, 67.94 and 36.63 MHz, respectively.

^1H NMR experiments of **1–4** were performed at 30°C, unless otherwise stated, in 5 mm diameter NMR tubes for saturated CD_2Cl_2 solutions. Because the solubility of compound **5** in CD_2Cl_2 was very small, it was measured in saturated $(\text{CD}_3)_2\text{CO}$ solution. The spectral width in ^1H experiments was 1000 Hz, number of data points 32000 giving 0.06 Hz digital resolution, acquisition time 16.4 s, number of scans 8–100 and flip angle 90° (8.4 μs). FIDs were exponentially windowed by digital resolution prior to Fourier transformation (FT) to improve the ratio signal/noise (S/N) in the frequency spectra. All ^1H NMR chemical shifts are internally referenced to tetramethylsilane, TMS.

^{13}C NMR experiments on **1–4** were performed at 30°C in 5 mm diameter NMR tubes in saturated CD_2Cl_2 solutions and for **5** and **6** in saturated $(\text{CD}_3)_2\text{CO}$ solutions. The spectral width in ^{13}C experiments was 16000 Hz, number of data points 64000 giving 0.5 Hz digital resolution, acquisition time 2.0 s, pulse delay 4 s, number of scans varied from 100 to 400. The clusters **5** and **6** required overnight accumulation, number of scans > 8000, and pulse delay was lifted to 10 s in order to observe also the slowly relaxing interstitial carbons. For proton coupled spectra, number of scans was > 1000. Flip angle was 90° (8.8 μs). The FIDs were exponentially windowed by digital resolution prior to Fourier transformation (FT) to improve S/N in the frequency spectra. All ^{13}C NMR chemical shifts are internally referenced to TMS.

^{17}O NMR experiments on **1–4** were performed at 30°C in 10 mm diameter NMR tubes for saturated CD_3CN and CDCl_3 solutions and for **5** and **6** in saturated $(\text{CD}_3)_2\text{CO}$ solutions. The spectral width in ^{17}O experiments was 36000 Hz, number of data points 8000 giving a 10 Hz digital resolution, acquisition time 0.1 s with no pulse delay, number of scans was > 150000 and flip angle 90° (20.0 μs). The FIDs were exponentially windowed by digital resolution prior to Fourier

TABLE 1. ^1H NMR chemical shifts, ppm from TMS for 1–5

	Solvent	$\delta(\text{CH}_3)$	$\delta(\text{H aryl})$	ref.
1	$(\text{CD}_3)_2\text{CO}$	2.19	5.18	4
	CD_2Cl_2	2.17	4.93	
2	CD_2Cl_2	2.42 (2.17 ^a)	5.18 (4.94 ^a)	
3	CD_2Cl_2	2.50	5.93	
4	$(\text{CD}_3)_2\text{CO}$	2.53	6.23	4
	CD_2Cl_2	not obs ^b	not obs ^b	
5	$(\text{CD}_3)_2\text{CO}$	2.38	5.72	

^a Weak signal, whose origin is not clear. ^b Co-cluster 4 gave only very poorly resolved ^1H spectrum in CD_2Cl_2 .

transformation (FT) to improve S/N in the frequency spectra. All ^{17}O NMR chemical shifts are referenced to the signal of an external D_2O ($\delta = 0$ ppm) tube inserted coaxially inside the NMR tube. These shifts are uncorrected for the ^2H isotopic shift of -3 ppm [10].

3. Results and discussion

The ^1H chemical shifts, ^{13}C chemical shifts ($^1J(\text{C}, \text{H})$ coupling constants), and ^{17}O NMR chemical shifts are collected in Tables 1, 2 and 3, respectively. The structures of compounds 4–6 are described in Fig. 1.

A general feature of the ^1H NMR chemical shifts (Table 1) of all the compounds studied, is the clear shielding of all aromatic protons of mesitylene moiety in comparison with uncomplexed mesitylene, $\delta = 6.64$ ppm [11], in agreement with the values observed earlier for the related organometallic π -complexes [2,4].

The ^1H NMR chemical shifts of the aromatic protons of the mesitylene moiety in the chromium and tungsten complexes measured show only a difference of 0.25 ppm [$\delta(\text{W-complex})$ 5.18 ppm; $\delta(\text{Cr-complex})$

TABLE 3. ^{17}O NMR chemical shifts δ , ppm, from the signal of the external D_2O and ^{17}O NMR line widths L, Hz, of compounds 1–6 measured at 30°C

	$\delta(^{17}\text{O})/L$		
	CH_3CN	CDCl_3	$(\text{CD}_3)_2\text{CO}$
1	370.5 ^a /50	371.5/50	–
2	347.8/50	348.5/50	–
3	386.7/50	not obs	–
4	350.9 ^b	not obs	–
5	not obs	not obs	394.2/100
6	not obs	not obs	394.2/100

^a At 60°C 371.7 ppm. ^b Very broad signal, $L > 500$.

4.93 ppm]. Mesitylene tricarbonyl manganese (3) shows a ^1H chemical shift value ($\delta = 5.93$ ppm) that is clearly less shielded than 1 and 2. The cluster compound 4 containing cobalt exhibits the most deshielded value ($\delta = 6.23$ ppm) differing only slightly from that of the uncomplexed mesitylene [11], while in the ruthenium cluster (5) the shift is again more shielded being 5.72 ppm.

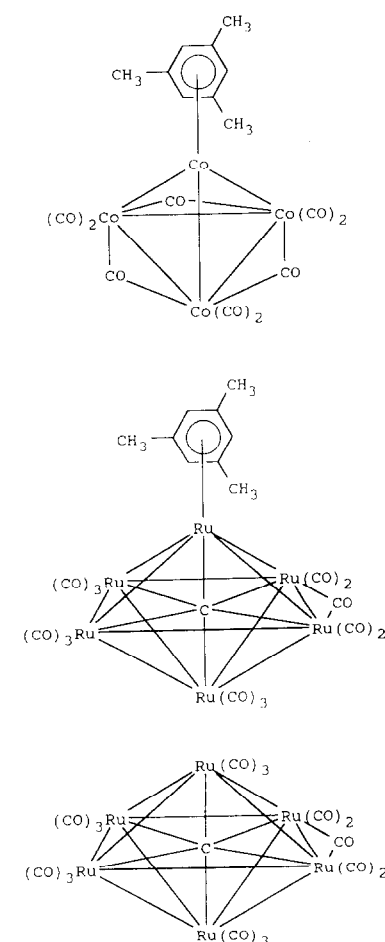


Fig. 1. Structures of transition metal carbonyl clusters 4–6.

TABLE 2. ^{13}C NMR chemical shifts δ , ppm from TMS and $^1J(\text{C}, \text{H})$ coupling constants, Hz, of compounds 1–6 measured at 30°C for saturated solutions in CD_2Cl_2

	$\delta(\text{CH}_3)/^1J$	$\delta(\text{C-H})/^1J$	$\delta(\text{C-CH}_3)$	$\delta(\text{CO})$	ref.
1	21.0	92.4	111.5	235.1	4
	21.2/129.1	93.0/171.2	112.1	235.1	
2	21.0/129.1	91.4/173.1 ^a	111.5 ^b	213.3	
3	21.0	96.4	101.3	202.4 ^c	
4	19.6	93.8	107.3	206.6	4
	20.3	94.5	108.0	not obs	
5	20.2 ^d	95.1 ^d	108.7 ^d	not obs ^d	4
	23.3 ^{c,e}	92.3	105.8	198.2 ^f	
6	–	–	–	198.2 ^f	

^a $^2J(\text{C}, \text{H}) = 4.9$ Hz. ^b $^3J(\text{C}, \text{H}) = 4.9$ Hz. ^c Required overnight accumulation (> 8000 scans) for proton noise decoupled ^{13}C NMR spectrum. ^d Measured in $(\text{CD}_3)_2\text{CO}$, C=O overlaps with the signal of $(\text{CD}_3)_2\text{CO}$. ^e Measured in $(\text{CD}_3)_2\text{CO}$, this compound did not give reliable signals in CD_3CN and CDCl_3 owing to low solubility. ^f Interstitial carbon not observed.

In order to explain these findings the internal architecture of the complexes and the anisotropy of the metal–arene bond should be taken into account [4]. In addition to the diamagnetic screening effects mentioned previously [2], the perturbations of the π -electron density induced by changes in σ -electron density are also effective (ref. 1, p. 14).

The ^1H NMR shifts of the methyl groups within each compound are similarly equivalent with those of the aromatic groups revealing that the axial symmetry of the arene is maintained during complexation or that the signal is a time average of a fast rotating aryl moiety. The deviations from the value of the methyl groups of the uncomplexed mesitylene ($\delta = 2.22$ ppm) [11] are clearly smaller than those of the aromatic signals. Further, there exists in this series of compounds a clear correlation between the ^1H NMR chemical shifts of aryl protons and those of methyl protons suggesting the same origins for the chemical shift changes in both types of protons in the mesitylene moieties.

In ^{13}C NMR chemical shifts there does not exist such a clear correlation between the aryl and methyl ^{13}C NMR chemical shifts as observed in ^1H NMR chemical shifts. In compounds **1–3** the values 93.0/91.4/96.4 (C^*-H) *vs.* 112.1/111.5/101.3 (C^*-CH_3) merely imply an inverse relation between the chemical shifts of these two type of carbons. The ^{13}C NMR chemical shifts of carbonyl carbons, being 235.1/213.3/202.4 ppm ($\text{C}^*=\text{O}$), are by no means related with those of the methyl or aryl carbons. Generally, these findings suggest different origins for the ^{13}C NMR chemical shifts of different types of carbons. However, as in the case of ^1H NMR chemical shifts, all aromatic ^{13}C NMR chemical shifts show clearly shielded values in comparison with the uncomplexed mesitylene. This effect might be due to the diamagnetic shift induced by metal valence electrons [2] and/or by σ -effects (ref. 1, p. 14) as in the case of proton chemical shifts. One should remember, however, that the main contribution of carbon chemical shifts is explained by the paramagnetic screening factor dependent on, for example, the average excitation energy and bond orders [3]. In addition, the nuclear size and net charge also should be taken into account [3]. Therefore, the clarification of the significance of all these factors is a very complicated task, but it is in principle possible by comparison of the NMR data obtained from various atoms and NMR nuclei.

The interstitial carbon included in the structure **5** and **6** is very rare and is therefore interesting. Attempts to observe the ^{13}C NMR chemical shift of that carbon in these clusters were, however, unsuccessful.

The special features of the ^{13}C NMR chemical shifts

of the carbonyl groups in organometallic compounds generally are explained by the backdonation of the metal d-orbitals to the π^* -orbitals of the carbonyl group [3]. The ^{13}C NMR chemical shift changes of the carbonyl groups in compounds studied are in agreement with a previous study by Hickey *et al.* [3]. They argued that the ^{13}C NMR chemical shifts become more shielded with increasing nuclear size and in going from neutral to isostructural cationic complex. This trend can be seen clearly when the chemical shifts of compounds **1–3** (235.1, 213.3 and 202.4 ppm) are compared.

The ^{13}C NMR chemical shifts of the corresponding metal carbonyls are for $\text{Cr}(\text{CO})_6$, $\text{W}(\text{CO})_6$, $\text{Mn}_2(\text{CO})_{10}$, $\text{Co}_2(\text{CO})_8$; 212.5, 192.1, 212.9 (*cis*)/223.1 (*trans*), 203.2 [12], and for $\text{Ru}(\text{CO})_4\text{H}_2$; 192.6/190.4 (ref. 1, p. 173), respectively. The ^{13}C NMR chemical shifts of the carbonyl groups in the present mesitylene tricarbonyl metal complexes of Cr ($\delta = 235.1$ ppm) and W ($\delta = 213.3$ ppm) also correlate with the corresponding metal carbonyl chemical shifts as expected, showing only more deshielded values. The CO chemical shift of compound **3** ($\delta = 202.4$ ppm) is much smaller than those of manganese carbonyls given above, while the clusters **5** and **6** give a value of 198.2 ppm, which is somewhat higher value than those of ruthenium carbonyls.

$^1J(\text{C}, \text{H})$ coupling constants of methyl groups, 129.1 Hz, show values typical for sp^3 -hybridised carbon (ref. 2, p. 376). The aromatic $^1J(\text{C}, \text{H})$ coupling constants being > 170 Hz, however, are increased in comparison with the $^1J(\text{C}, \text{H})$ aryl carbons (ref. 2, p. 376) revealing the increased s-orbital character in C–H bonds. This may be connected with a σ -effect parallel with the changes also in the chemical shifts.

This is as far as we know the first time ^{17}O NMR spectroscopy has been utilized in studying a series of mesitylene carbonyl transition metal complexes and clusters. The present ^{17}O NMR spectra measured at 30°C show only one sharp resonance line/compound (similarly with ^{13}C NMR chemical shifts) the line width being generally < 100 Hz. All attempts to observe separate signals originated from the different carbonyls below the fast exchange limit failed, probably due to low solubility of the samples.

The ruthenium clusters **5** and **6** showed particularly low solubility in all solvents studied. Acetone- d_6 was the only one, in which ^{17}O and ^{13}C NMR spectra could be obtained after overnight accumulation. For checking the reliability of the signals observed, the solvent itself was measured under the same conditions as the real samples and using the same number of pulses. Acetone- d_6 gave only one peak in the carbonyl region in ^{17}O and ^{13}C experiments at 582.8 and 205.8 ppm respectively.

The ^{17}O NMR chemical shifts of the present carbonyl complexes are in the range of 340–400 ppm from the water signal, which is similar to the other arene (such as toluene) carbonyl transition metal complexes [3]. ^{17}O NMR chemical shifts of metal carbonyls (refs. 1 and 13, p. 28) and some acyl derivatives (ref. 13, p. 27) are also comparable with the present values, which are substantially smaller than those of ketones and aldehydes (ref. 13, p. 26).

The situation in which all the carbonyls give only one signal could arise from molecular symmetry, by very small differences in chemical shifts, which seems improbable owing to the large chemical shift difference of the terminal and bridged carbonyl ^{17}O resonances (ref. 1, p. 15) or by the fast exchange conditions in the ^{17}O NMR timescale.

Regarding the relation which holds for common organic molecules between the ^{17}O NMR line width and molecular size (reorientation time) [13], the ^{17}O NMR lines of the present complexes are surprisingly sharp and thus suggest rapid interconversion of all CO ligands [4].

Hickey *et al.* [3] have studied some related systems containing toluene, *o*-, *m*- and *p*-xylene $\text{W}(\text{CO})_3$ complexes *etc.*, but not mesitylene. Comparison between the present study and that mentioned above [3] shows that the values of mesitylene/toluene complexes are very similar, being for the Cr-complex 370.5/370.0 and for the W-complex 347.8/345.9 ppm, respectively. In the present mesitylene series of complexes, the cationic manganese compound **3** shows the most markedly deshielded chemical shift, $\delta = 386.7$ ppm. The cluster **4** shows a singlet line at 350.9 ppm which is clearly broader (> 500 Hz) than the other compounds. Attempts to resolve the spectrum into the separate lines respectively originating from the different carbonyls below the coalescence temperature also failed with this cluster.

Both ruthenium clusters **5** and **6** gave exactly the same ^{17}O carbonyl chemical shift $\delta = 394.2$ ppm (their ^{13}C NMR chemical shifts were similarly the same being $\delta = 198.2$ ppm). Thus the mesitylene moiety does not seem to affect the chemical shifts of the carbonyls of **5**. This is probably because in **5** the ruthenium atom bound to the mesitylene moiety does not bind any carbonyls directly (see Fig. 1).

The opposing trends in the $^{17}\text{O}/^{13}\text{C}$ NMR chemical shifts of CO resonances in the present compounds have been explained [3] by the backdonation of metal *d*-orbital to the π^* -orbital of CO. This tendency, however, is accompanied by many other effects and cannot be utilized in more far reaching discussions in the present case. The lack of response of ^{17}O NMR chemical shifts of the carbonyl groups of the compounds

under consideration to change of solvent indicates that the latter do not show any particular tendency to coordinate with the carbonyl oxygen of the complexes studied.

4. Conclusions

The present series of 1,3,5-trimethylbenzene (mesitylene) carbonyl transition metal compounds: mesitylene tricarbonyl chromium, $(\text{CH}_3)_3\text{C}_6\text{H}_3\text{Cr}(\text{CO})_3$ (**1**), mesitylene tricarbonyl tungsten, $(\text{CH}_3)_3\text{C}_6\text{H}_3\text{W}(\text{CO})_3$ (**2**), mesitylene tricarbonyl manganese tetrafluoroborate, $[(\text{CH}_3)_3\text{C}_6\text{H}_3\text{Mn}(\text{CO})_3]\text{BF}_4$ (**3**), and clusters, mesitylene nonacarbonyl tetracobalt, $(\text{CH}_3)_3\text{C}_6\text{H}_3\text{Co}_4(\text{CO})_9$ (**4**), mesitylene carbido tetradecacarbonyl hexaruthenium, $(\text{CH}_3)_3\text{C}_6\text{H}_3\text{Ru}_6\text{C}(\text{CO})_{14}$ (**5**) and carbido heptadecacarbonyl hexaruthenium, $\text{Ru}_6\text{C}(\text{CO})_{17}$ (**6**) forms an interesting topic for multinuclear magnetic resonance spectroscopy, as there are only a very few previous studies in this field of arene carbonyl transition metal complexes.

The ^1H and ^{13}C NMR chemical shifts of the mesitylene moieties are characterized by increased shieldings, which might be caused by diamagnetic screening of the metal valence electrons.

Regarding the carbonyl groups, their ^{13}C NMR chemical shifts follow known rules concerning nuclear size and charge. The opposing trends in ^{13}C vs. ^{17}O NMR chemical shifts can be explained by the π -back donation properties of the metal *d*-electrons.

The $^1J(\text{C}, \text{H})$ coupling constants in aromatic C–H bonds of mesitylene metal carbonyls are clearly increased compared with uncoordinated arenes. This increased s-character in the bond can be explained by a transition metal-induced σ -effect, which disturbs the whole π -system of the arene.

Three, or even more in favourable cases, different NMR nuclei included in the structures of transition metal mesitylene carbonyls provide three different points of view on their structures and properties. In this work all three NMR nuclei utilized gave spectra characterized by fast exchange limit giving only one line per type of atom. By comparing the results from different nuclei, it was possible to draw qualitative conclusions concerning the relative importances of different intramolecular effects.

The low solubility of organometallic carbonyls is often a serious limiting factor and therefore some ^{17}O enrichment studies may be necessary. In spite of that, the ^{17}O NMR experiments at natural abundance can also provide useful information owing to the very favourable line widths and sensitivity in comparison with common organic compounds of the same molecular size.

References

- 1 B.E. Mann and B.F. Taylor, *¹³C NMR Data for Organometallic Compounds*, Academic Press, 1981, pp. 151–182 and references cited therein.
- 2 H. Günther, *NMR Spectroscopy—an Introduction*, John Wiley, 1987, p. 91.
- 3 J.P. Hickey, J.R. Wilkinson and L.J. Todd, *J. Organomet. Chem.*, **179** (1979) 159 and references cited therein.
- 4 V.S. Kaganovich and M.I. Rybinskaya, *J. Organomet. Chem.*, **344** (1988) 383 and references cited therein.
- 5 (a) S. Aime, L. Milone, D. Osella, G.E. Hawkes and E.W. Randall, *J. Organomet. Chem.*, **178** (1979) 171; (b) S. Aime, L. Milone, D. Osella, G.E. Hawkes and E.W. Randall, *J. Am. Chem. Soc.*, **103** (1981) 5920; (c) S. Aime, L. Milone, D. Osella and E. Sappa, *Inorg. Chim. Acta*, **29** (1978) L211.
- 6 A.N. Nesmeyanov, M.I. Rybinskaya and V.S. Kaganovich, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1978) 2824 (in Russian).
- 7 A.N. Nesmeyanov, V.V. Krivykh, V.S. Kaganovich and M.I. Rybinskaya, *J. Organomet. Chem.*, **102** (1975) 185.
- 8 M.I. Rybinskaya, V.S. Kaganovich and A.R. Kudinov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1984) 885 (in Russian).
- 9 V.S. Kaganovich, Z.A. Kerzina, T. Asunta, K. Wickström and M.I. Rybinskaya, *J. Organomet. Chem.*, **421** (1991) 117.
- 10 I.P. Gerothanassis and J. Lauterwein, *Magn. Reson. Chem.*, **24** (1986) 1034 and references cited therein.
- 11 F.A. Bovey, *Nuclear Magnetic Resonance Spectroscopy*, Academic Press, New York, 1969, p. 257.
- 12 E. Breitmaier and W. Voelter, *Carbon-13 NMR Spectroscopy*, 3rd edition, VCH Verlagsgesellschaft mbH, Weinheim, 1987, p. 294.
- 13 J.-P. Kintzinger, in P. Diehl, E. Fluck and R. Kosfeld (eds.), *Oxygen NMR. Characteristic Parameters and Applications in NMR 17. Oxygen-17 and Silicon-29. Basic Principles and Progress*, Springer Verlag, Berlin, 1981, p. 40.