Mono-, bi- and polynuclear complexes of diphenylmethane with Cr, Co and Ru. Synthesis and investigation by ^{1}H, ^{13}C and ^{17}O NMR *

E. Kolehmainen [a,*], K. Laihia [a], J. Korvola [a], V.S. Kaganovich [b], M.I. Rybinskaya [b], Z.A. Kerzina [b]

[a] Department of Chemistry, University of Jyväskylä, PO Box 35, FIN-40351 Jyväskylä, Finland
[b] A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov Str. 28, 117813 Moscow, Russia

Abstract

Complexes of diphenylmethane (Ph_2CH_2): $Ph_2CH_2Cr(CO)_3$ (1), $Ph_2CH_2[Cr(CO)_3]_2$ (2), $Ph_2CH_2Co_4(CO)_9$ (3), $Ph_2CH_2[Co_4(CO)_9]_2$ (4), $Ph_2CH_2Cr(CO)_3Co_4(CO)_9$ (5) and $Ph_2CH_2Ru_6C(CO)_{14}$ (6) have been prepared and characterized by ^{1}H and ^{13}C- and ^{17}O-NMR spectroscopy. Strong shielding effects are caused by the metal valence electrons on the ^{1}H- and ^{13}C-NMR chemical shifts of aromatic protons and carbons in π-coordinated ring(s) of diphenylmethane. Generally, the order of these shielding effects on the nuclei of the aromatic rings in ^{1}H-NMR was $Co_4(CO)_9 < Ru_6C(CO)_{14} < Cr(CO)_3$ and in ^{13}C-NMR $Co_4(CO)_9 < Cr(CO)_3 < Ru_6C(CO)_{14}$. In addition, aromatic solvent exhibits an enhanced shielding effect on the ^{1}H-NMR chemical shifts of the π-coordinated ring induced probably by aromatic solvent induced shifts (ASIS). The ^{1}H-NMR chemical shifts of the exocyclic methylene protons are shielded or deshielded depending on the solvent, the metal and the degree of π-coordination. These findings can be explained by the varying conformational states adopted by the flexible ligand. The ^{13}C-NMR chemical shifts of the methylene carbon are generally shielded supporting the above explanation. This conformational flexibility can be of extreme importance in controlling the catalytic activity of these organometallic compounds. In chromium and heterobimetallic chromium cobalt derivatives 1, 2 and 5, ^{17}O-NMR spectroscopy proved to have excellent sensitivity comparable with that of ^{13}C-NMR. In cobalt clusters 3 and 4 no ^{17}O-NMR lines were observed, which is probably because of strongly broadened ^{17}O-NMR signals of carbonyls undergoing dynamic exchange. In the ruthenium cluster 6 only one broad ^{17}O-NMR line at 30°C was observed. An inverse relation between the ^{13}C- and ^{17}O-NMR chemical shifts of the carbonyl groups can be explained by the effect of π-backbonding.

Keywords: Chromium; Cobalt; Ruthenium; Arene; Carbonyl; Nuclear magnetic resonance

1. Introduction

Transition metal (Cr, W and Mn) tricarbonyls and transition metal (Ru and Co) carbonyl clusters π-coordinated with monoarenes such as toluene and mesitylene were previously characterized by multinuclear magnetic resonance spectroscopy [1–3]. In addition to ^{13}C-NMR spectroscopic data, which have been collated exhaustively by Mann and Taylor [3], ^{17}O-NMR reveals

easy-to-detect spectral characteristics [1,4,5]. Recently, interest in transition metal carbonyl complexes of polyaromatic hydrocarbons has developed [6,7]. This prompted us to continue synthetic and multinuclear magnetic resonance spectroscopic studies on transition metal carbonyl complexes of polyarene-type ligands. In the present work, this kind of derivative of diphenylmethane has been studied. Generally, π-coordination in polyarene compounds can offer very large structural variation when preparing mono- and homo/heterobimetallic complexes or clusters. The conformational flexibility of the ligand, as in diphenylmethane, can also offer interesting possibilities for control of the properties of these organometallics. NMR spec-

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troscopy is certainly one of the most efficient methods for these studies. Further, these new transition metal derivatives may possess extraordinary catalytic and chemical properties in comparison with the monoaromatic derivatives.

2. Experimental section

2.1. Syntheses

All reactions were carried out in argon atmosphere using absolutely dry solvents. The work up of the products was performed using standard solvents and without precautions being taken to exclude air.

Diphenylmethane tricarbonyl chromium, $(C_6H_5)_2$-$CH_2Cr(CO)_3$ (1) was obtained according to the method detailed in Ref. [8], the yield of 1 being improved to 58%.

Diphenylmethane hexacarbonyl dichromium, $(C_6H_5)_2CH_2[Cr(CO)_3]_2$ (2). A mixture of 800 mg (1.82 mmol) of $Cr(CO)_6$ and 300 mg (1.78 mmol) of Ph_2CH_2 was refluxed in 50 ml of diglyme + 10 ml of heptane for 5 h. After cooling the solvent was evaporated in vacuo. The residue was chromatographed on an Al_2O_3 column using a CH_2Cl_2/petrol ether $(v/v, 1/1)$ mixture as an eluent giving two yellow fractions, 1 (42%) and 2 (14%), respectively. 2 was recrystallized from CH_2Cl_2 containing 10% heptane. The melting point of 2 is 143–145°C (decomp.). Elemental analysis for $C_{19}H_{12}$-Cr_2O_6: found (calculated), C 51.69 (51.83), H 2.81 (2.75), Cr 23.69 (23.62)%. IR spectrum: $\nu(C \equiv O)$ 1961, 1892 cm^{-1} (in CH_2Cl_2).

Diphenylmethane nonacarbonyl tetracobalt, $(C_6H_5)_2CH_2Co_4(CO)_9$ (3) was obtained according to the usual method [8].

Diphenylmethane octadecacarbonyl octacobalt, $(C_6H_5)_2CH_2[Co_4(CO)_9]_2$ (4) was obtained according to the usual method [8]. The X-ray crystal structure of 4 has also been determined [9].

Diphenylmethane tricarbonyl chromium nonacarbonyl tetracobalt, $(C_6H_5)_2CH_2Cr(CO)_3Co_4(CO)_9$ (5) was obtained according to Ref. [8].

Diphenylmethane carbido tetradecacarbonylhexaruthenium, $(C_6H_5)_2CH_2Ru_6C(CO)_{14}$ (6). A mixture of 300 mg (0.47 mmol) of $Ru_3(CO)_{12}$ and 500 mg (2.96 mmol) of Ph_2CH_2 was refluxed in 60 ml of octane for 14 h. After cooling the mixture was chromatographed on a SiO_2 column using mixtures of CH_2Cl_2/petrol ether with growing polarity. The third, brown band gave 16.5 mg (6%) of 6. The product was recrystallized from CH_2Cl_2/hexane $(v/v, 1/10)$. The product decomposed without melting at 160–170°C. Elemental analysis for 6 ($C_{28}H_{12}O_{14}Ru_6$): found (calculated), C 28.21 (28.53), H 1.53 (1.03) %. IR spectrum: $\nu(C \equiv O)$ 2074m, 2061w, 2038m sh, 2013s, 1994w, 1982w, 1968w,

1827w cm^{-1} (in heptane). Mass spectrum. $[m/e]^+$: very complex pattern of peaks from 1166 to 1193 (with intensity $> 5\%$ when the greatest peak at 1181 is 100%) characteristic for ruthenium with seven stable isotopes (calc. 1179), $[M - CO]^+$ (weak), $[M - 2CO]^+$ (very weak), $[M - 3CO]^+$ (strong) etc. — successive loss of 14 carbonyl groups up to $[M - 14CO]^+ = 786$ were observed.

2.2. Spectroscopy

IR spectra of the products were recorded on a Specord 75IR spectrometer.

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

^{1}H-NMR experiments were performed at 30°C in 5 mm diameter NMR tubes for saturated $CDCl_3$ solutions unless otherwise stated. The spectral width in ^{1}H experiments was 3500 Hz and the number of data points 32000 giving 0.21 Hz digital resolution. The acquisition time was 4 s, number of scans 16 and flip angle 90° (8.4 μs). The FIDs were exponentially windowed by digital resolution prior to Fourier transformation (FT) to improve the signal/noise ratio (S/N) in the frequency spectra. All ^{1}H-NMR chemical shifts are internally referenced to tetramethylsilane.

^{13}C-NMR experiments were performed at 30°C in 5 mm diameter NMR tubes for saturated $CDCl_3$ solutions using proton broad band decoupling (BBD) pulse sequence. The spectral width in ^{13}C experiments was 15000 Hz and the number of data points 32000 giving 0.92 Hz digital resolution. The acquisition time was 1 s, pulse delay 3 s, number of scans 100–1000 and flip angle 90° (7.7 μs). The FIDs were exponentially windowed by digital resolution prior to Fourier transformation (FT) to improve the signal/noise ratio (S/N) in the frequency spectra. All ^{13}C-NMR chemical shifts are internally referenced to TMS.

^{17}O-NMR experiments were performed at 30°C in 10 mm diameter NMR tubes for saturated $CDCl_3$: $CHCl_3$ (1 : 3) solutions using proton broad band decoupling (BBD) pulse sequence. The spectral width in ^{17}O experiments was 36000 Hz and the number of data points 8000 giving 9 Hz digital resolution. The acquisition time was 0.1 s without any pulse delay, number of scans 20000–100000 and flip angle 90° (20.0 μs). The 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 ^{17}O-NMR chemical shifts are referenced to the signal of an external H_2O tube inserted coaxially inside the NMR tube.

The mass spectrum of 6 was obtained with a VG AutoSpec mass spectrometer using direct inlet and 35 eV ionization potential.

Table 1

^{1}H- and ^{17}O-NMR data of chromium, cobalt and ruthenium carbonyl complexes and clusters with diphenylmethane (L) at 30°C in CDCl$_3$

	Compound	$\delta(^1H)$, [a] ppm							$\delta(^{17}O)$, [b] ppm
		Noncoordinated ring			π-coordinated ring			CH_2	CO
		H-2/6	H-3/5	H-4	H-2/6	H-3/5	H-4		
	L	7.17	7.24	7.16	–	–	–	3.95	–
	L [c]	7.00	7.06	7.00	–	–	–	3.71	–
1	LCr(CO)$_3$	7.23	7.30	7.22	5.16	5.33	5.16	3.70	373.6
	LCr(CO)$_3$ [c]	7.0 [d]	7.0 [d]	7.0 [d]	4.4 [d]	4.4 [d]	4.4 [d]	3.22	not obs
2	L[Cr(CO)$_3$]$_2$	–	–	–	5.26	5.35	5.3	3.44	373.5
3	LCo$_4$(CO)$_9$	7.00	7.21	7.2 [d]	6.17	6.07	6.1 [d]	4.24	not obs
	LCo$_4$(CO)$_9$ [e]	7.01	7.21	7.2 [d]	6.21	6.11	6.1 [d]	4.25	not obs
	LCo$_4$(CO)$_9$ [c]	7.1–6.6	7.1–6.6	7.1–6.6	5.55	5.32	5.43	3.97	not obs
	LCo$_4$(CO)$_9$ [f]	7.2 [d]	7.2 [d]	7.2 [d]	6.54	6.37	6.46	4.34	not obs
4	L[Co$_4$(CO)$_9$]$_2$	–	–	–	5.96	6.04	6.14	4.53	not obs
5	LCr(CO)$_3$Co$_4$(CO)$_9$	–	–	–	4.94	5.20	5.17	3.98	377.3 [g]
		–	–	–	6.20	6.15	6.28		not obs [h]
6	LRu$_6$C(CO)$_{14}$	7.1	7.3 [d]	7.3 [d]	5.6	5.6	5.24	3.49	394 [i]

[a] From internal TMS.
[b] From external H$_2$O.
[c] Measured in toluene-d_8.
[d] Strongly overlapping signals.
[e] Measured in CD$_2$Cl$_2$.
[f] Measured in acetone-d_6.
[g] Cr-coordinated ring.
[h] Co-coordinated ring.
[i] Broad signal.

3. Results and discussion

The structures of the compounds 1–6 are described in Fig. 1 and their ^{1}H-, ^{17}O- and ^{13}C-NMR chemical shifts are collected in Tables 1 and 2.

The ^{1}H- and ^{13}C-NMR chemical shifts of π-coordinated rings in chromium compound 1, cobalt cluster 3 and ruthenium cluster 6 are easily separated from those of the noncoordinated ring via strong shielding effects allied with the coordination and caused by the

diamagnetic screening of the metal valence electrons [1,2,10]. These effects are useful for assigning the ^{1}H- and ^{13}C-NMR spectra of the compounds studied.

3.1. ^{1}H-NMR

The ^{1}H-NMR chemical shifts of the aromatic protons of the non-coordinated ring are only slightly influenced by the π-coordinated neighbouring ring. For example, in 1 the proton shifts are deshielded by only

Table 2

^{13}C-NMR chemical shifts of chromium, cobalt and ruthenium carbonyl complexes and clusters with diphenylmethane (L) at 30°C in CDCl$_3$

	Compound	$\delta(^{13}C)$, [a] ppm									
		Noncoordinated ring				π-coordinated ring				CH$_2$	CO
		C-1	C-2/6	C-3/5	C-4	C-1	C-2/6	C-3/5	C-4		
	L [b]	141.3	129.0	128.5	126.2	–	–	–	–	42.1	–
	L	141.10	128.93	128.43	126.04	–	–	–	–	41.94	–
	L [c]	141.39	129.21	128.60	126.23	–	–	–	–	42.13	–
1	LCr(CO)$_3$	138.25	128.82	128.82	127.10	112.43	93.51	93.04	90.78	40.75	233.0
	LCr(CO)$_3$ [c]	138.83	128.9	128.9	127.43	112.39	93.41	92.75	90.30	40.83	not obs
2	L[Cr(CO)$_3$]$_2$	–	–	–	–	108.50	92.92	92.60	91.59	39.51	232.4
3	LCo$_4$(CO)$_9$	138.86	128.89	128.41	127.11	112.14	94.82	93.93	93.93	40.44	not obs
4	L[Co$_4$(CO)$_9$]$_2$	–	–	–	–	109.07	94.36	93.94	not obs	38.38	not obs
5	LCr(CO)$_3$Co$_4$(CO)$_9$	–	–	–	–	108.50	92.74	91.73	94.70	38.69	232.0 [d]
						108.79	94.82	94.00	not obs		not obs [e]
6	LRu$_6$C(CO)$_{14}$	138.76	129.22	128.25	127.64	107.20	90.80	87.33	86.32	42.01	202 [f]

[a] From internal TMS.
[b] Values taken from Ref. 12, p. 256.
[c] Measured in toluene-d_8.
[d] Cr-coordinated ring.
[e] Co-coordinated ring.
[f] Broad signal W$_{1/2}$ > 200 Hz.

0.06 ppm in $CDCl_3$ and shielded by 0.06 ppm (H-3/5) in toluene-d_8, consistent with the π-coordination of chromium tricarbonyl at the neighbouring ring. The corresponding effects observed in the ^1H-NMR chemical shifts of the noncoordinated ring in the compounds **3** and **6** are also small. Consequently, the transmission of electronic effects between the rings caused by the π-coordination is not significant. From the synthetic point of view this means that the formation of a bicoordinated derivative from the monocoordinated complex is not strongly inhibited by any unfavourable change in the π-system of the noncoordinated ring.

The ^1H-NMR chemical shifts of the methylene protons are sensitive to the solvent, the π-coordinated metal and the degree of coordination. For example, the methylene protons are shielded 0.25 ppm in **1** and 0.51 ppm in **2** but deshielded 0.29 ppm in **3** and 0.58 ppm in **4**, respectively. Further, toluene induces an enhanced shielding effect of 0.48 ppm (or 0.73 ppm from the value of the ligand) on the methylene protons of **1** and 0.27 ppm on those of **3**.

In order to clarify the origin of these effects, they have been measured in different solvents for the monometallic derivatives **1** and **3**. As stated above, toluene exhibits extra-ordinary properties in comparison with all other solvents in that it clearly shields the protons of the π-coordinated ring. This can be explained by the aromatic solvent induced shift (ASIS) of the stacked solvent molecule(s) with diphenylmethane ligand. Acetone exhibited for **3** an opposite (deshielding) and smaller effect than toluene which can also be
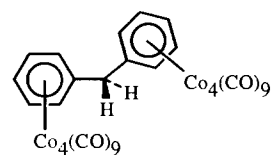
S-TRANS, S-TRANS

S-TRANS   S-CIS

Scheme 1.

explained by the anisotropy of the carbonyl group of the solvent.

Generally, the influence of the tricarbonyl chromium in **1**, nonacarbonyl tetracobalt **3** and tetradecacarbonyl carbido hexaruthenium in **6** on the aromatic protons is shielding (diamagnetic) as expected based on the general influence of metal valence electrons [10]. The metals differ only by the extent of the effect, the order being $Co_4(CO)_9 < Cr(CO)_3 < Ru_6C(CO)_{14}$. Based on these data alone one would expect that the methylene protons would follow the same shift order particularly because the inter-ring effects are negligible. As stated above, the methylene protons, however, show more complex behaviour than the aromatic ones. Therefore, it is reasonable to correlate the different behaviours of the methylene protons with some flexible parameter such as the conformational state of the ligand.

In cobalt clusters **3** and **4** the methylene protons show exceptional deshielded values when compared with all the other organometallics and with the ligand itself. According to the X-ray diffraction analysis [9], **4** has in the crystalline state a s-*trans*-s-*trans* conformation (see Scheme 1). In that structure the methylene protons are spatially close to both the cobalt carbonyl moieties. Because both of the clusters **3** and **4** show qualitatively similar behaviour differing only in the extent of the shift, one would suggest that the conformational state of **3** is also s-*trans* (see Scheme 1). Therefore, one would hypothesize that the conformational state of **1** and **6** is different, viz. s-*cis*, where the methylene protons are located at the same site as aromatic protons of the π-coordinated ring, consequent on the metal being thus shielded. It is not, however, totally excluded that this effect could be caused by the magnetic anisotropies differing between the different metal–carbonyl moieties ($Cr(CO)_3$ and $Co_4(CO)_9$), which are both in the s-*trans* conforma-
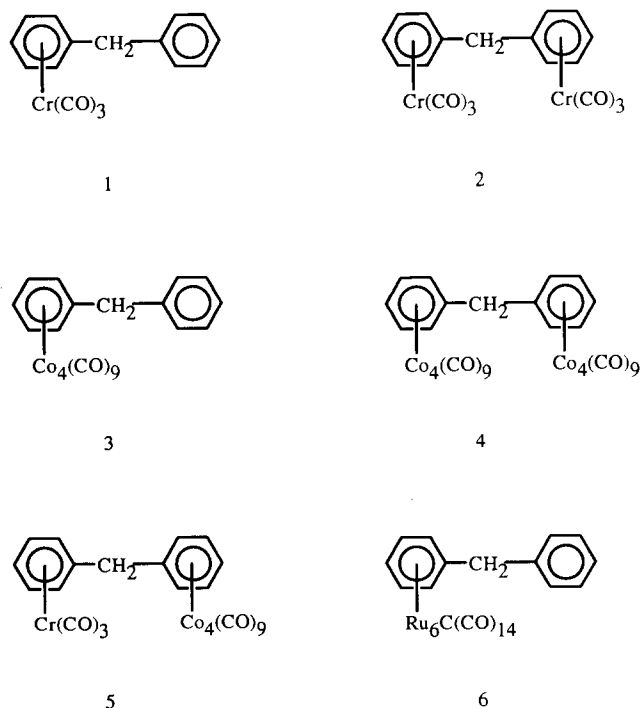

Fig. 1. Structures of compounds 1–6.

tional state. Owing to the small amounts of some samples and their slow decomposition at higher temperatures in solution, we did not manage to study systematically the temperature dependencies of their NMR spectra.

The clear shielding in ^{1}H-NMR chemical shifts observed in both **1** and **3**, induced by the aromatic solvent can be explained by the conformational state adopted by **1** and **3** in toluene being the same. This means that in toluene **3** should be transformed in the s-*cis* conformation in which there is no steric hindrance for the influence of the solvent molecules at the site of the methylene protons as there is in the s-*trans* form, due to the bulky cluster moiety.

The heterobimetallic derivative **5** represents in many respects an average of the homobimetallic derivatives **2** and **4**. For example, the ^{1}H-NMR chemical shift $\delta(CH_2) = 3.98$ ppm is exactly the mean value of those of **2** and **4**. This suggests that in **5** the conformational state of the methylene protons are the same in respect of both metal carbonyls as in **2** and **4**.

3.2. ^{13}C-NMR

As in the case of ^{1}H-NMR, the ^{13}C-NMR chemical shifts of aromatic carbons are strongly shielded at the π-coordinated ring owing to the diamagnetic effect of the metal valence electrons [10]. This finding can be utilized in the assignment of the chemical shifts. Double π-coordination generally still enhances the shielding, the influence of the second coordination step being much less than that of the first one. The small deshielding effects observed in ^{1}H-NMR for the non-coordinated rings of monometallic derivatives are visible only for carbons 3/5 and 4 of complex **1**, 4 of complex **3** and 2/6 and 4 of complex **6**. The *ipso*-carbon 1 of the noncoordinated ring is shielded 2.25–2.85 ppm consistent with the π-coordination at the neighbouring ring, the other carbons remaining almost unchanged.

The methylene carbons of the cobalt clusters **3** and **4** as observed in ^{1}H-NMR do not show such an exceptional behaviour. This fact supports the conclusion drawn above concerning the conformational differences between the compounds studied—the conformational changes do not change the position of the exocyclic carbon unlike what is observed with the methylene protons.

As in ^{1}H-NMR, in ^{13}C-NMR the heterobimetallic derivative **5** also represents an average of **2** and **4**. The ^{13}C-NMR chemical shift of 38.69 ppm of the methylene carbon of **5** is very close to the average of 38.95 ppm of the methylenes of **2** and **4**. Because the ^{1}H-NMR chemical shifts of the methylene protons of **5** also show a value intermediate between those of **2** and **4**, the positions of the metal carbonyl moieties in respect of the ligand of **5** are probably the same as in pure

homobimetallic compounds, being s-*trans* for the nonacarbonyl tetracobalt moiety.

The order of the shielding effects for the aromatic carbons of monometallic compounds **1**, **3** and **6** is $Co_4(CO)_9 < Cr(CO)_3 \ll Ru_6C(CO)_{14}$ while for the methylene carbons the order $Ru_6C(CO)_{14} < Cr(CO)_3 < Co_4(CO)_9$ is observed. Because of the weak transmission of the shielding effects via the CH_2-group, the carbon signals of the arene rings coordinated with different metals can be easily assigned. Thus, the resonance lines of the complex **5** (108.50, 92.74, 91.73 and 94.70 ppm) belong to the $Cr(CO)_3$ coordinated ring whereas the signals 108.79 94.82 and 94.00 ppm belong to the ring coordinated with the $Co_4(CO)_9$ cluster moiety.

All chromium tricarbonyl derivatives **1**, **2** and **5** gave clear carbonyl signals at $\delta(^{13}C \equiv O) = 232.0–233.0$ ppm. These values are close to those of mesitylene tricarbonyl chromium [1]. In cobalt derivatives **3** and **4** no carbonyl signal was observed probably owing to the dynamic exchange reaction under the intermediate rate regime. Therefore the carbonyl signal observed for **5** is most probably caused by the tricarbonyl chromium moiety. In the ruthenium cluster **6** only one broad signal at 202 ppm was observed representing the statistical mean of all different carbonyls, which can be resolved at lower temperatures in related structures [11]. Although it has been argued that the ^{13}C-NMR chemical shifts of CO groups in metal carbonyls become more shielded with increasing nuclear size of the metal [4], a direct comparison of **1** and **6** could be misleading owing to the very different structures of the metal carbonyl moieties.

3.3. ^{17}O-NMR

Compounds **1**, **2** and **5** containing tricarbonyl chromium moieties show very sharp $(W_{1/2} = 50$ Hz) ^{17}O-NMR lines as reported for the corresponding mesitylene complex [1]. In cobalt derivatives no signals were observed at 30°C. In **6** only one broad signal was found as in ^{13}C-NMR. A comparison of compounds **1** and **6** reveals that the ^{13}C- and ^{17}O-NMR chemical shifts of their carbonyl groups are inversely proportional probably because of the backdonation of metal d-orbital to the π^*-orbital of CO [4].

4. Conclusions

Diphenylmethane exhibits excellent synthetic properties for the preparation of transition metal carbonyl π-complexes and clusters. The presence of the two arene rings allows preparation of both mono- and homo/heterobimetallic derivatives. In this study diphenylmethane tricarbonyl chromium, Ph_2CH_2Cr-

(CO)$_3$ (**1**), diphenylmethane hexacarbonyl dichromium, Ph$_2$CH$_2$[Cr(CO)$_3$]$_2$ (**2**), diphenylmethane nonacarbonyl tetracobalt, Ph$_2$CH$_2$Co$_4$(CO)$_9$ (**3**), diphenylmethane octadecacarbonyl octacobalt, Ph$_2$CH$_2$[Co$_4$(CO)$_9$]$_2$ (**4**), diphenylmethane tricarbonyl chromium nonacarbonyl tetracobalt, Ph$_2$CH$_2$Cr(CO)$_3$Co$_4$(CO)$_9$ (**5**) and diphenylmethane carbido tetradecacarbonyl hexaruthenium, Ph$_2$CH$_2$Ru$_6$C(CO)$_{14}$ (**6**) have been synthesized.

Generally, the ^{1}H- and ^{13}C-NMR chemical shifts of the aromatic nuclei of diphenylmethane in mononuclear and cluster π-complexes, are characterized by increased shielding caused by diamagnetic screening of the metal valence electrons. In addition, the ^{1}H-NMR chemical shifts of the protons of the π-coordinated ring as well as of the exocyclic methylene protons depend clearly on the solvent. These findings can be understood by varying conformational state of the ligand controlled by π-coordinated metal and the solvent used.

The opposite trends in ^{13}C- vs. ^{17}O-NMR chemical shifts of the carbonyl groups can be explained by the π-back donation properties of the metal d-electrons. The ^{17}O-NMR experiments at natural abundance proved in the case of tricarbonyl chromium derivatives to be of special sensitivity, comparable with that of ^{13}C-NMR. This property could be very useful for characterizing the structures of polycyclic aromatic π-complexes and clusters to be prepared in the future.

Acknowledgements

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