

Mono-, bi- and polynuclear complexes of dimethyldiphenylsilane, diphenylether and biphenyl with Cr, Co and Ru. Synthesis and ^1H , ^{13}C , ^{17}O and ^{29}Si NMR spectroscopic characterization [☆]

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Abstract

Mono- and bimetallic transition metal carbonyls of dimethyldiphenylsilane, $\text{Ph}_2\text{Si}(\text{CH}_3)_2$ (L1), diphenylether, Ph_2O (L2) and biphenyl, Ph_2 (L3): $\text{Ph}_2\text{Si}(\text{CH}_3)_2\text{Cr}(\text{CO})_3$ (1), $\text{Ph}_2\text{Si}(\text{CH}_3)_2[\text{Cr}(\text{CO})_3]_2$ (2), $\text{Ph}_2\text{Si}(\text{CH}_3)_2\text{Co}_4(\text{CO})_9$ (3), $\text{Ph}_2\text{Si}(\text{CH}_3)_2[\text{Co}_4(\text{CO})_9]_2$ (4), $\text{Ph}_2\text{Si}(\text{CH}_3)_2\text{Cr}(\text{CO})_3\text{Co}_4(\text{CO})_9$ (5), $\text{Ph}_2\text{OCr}(\text{CO})_3$ (6), $\text{Ph}_2\text{OC}_4(\text{CO})_9$ (7), $\text{Ph}_2\text{ORu}_6\text{C}(\text{CO})_{14}$ (8), $\text{Ph}_2\text{OCr}(\text{CO})_3\text{Co}_4(\text{CO})_9$ (9) and $\text{Ph}_2\text{Ru}_6\text{C}(\text{CO})_{14}$ (10) have been prepared and characterized by means of ^1H , ^{13}C , ^{17}O and ^{29}Si NMR spectroscopy. The same order of the shielding effects induced by the transition metal ($\text{Co} < \text{Ru} < \text{Cr}$) on the ^1H NMR chemical shifts of the η^6 -coordinated ring as observed earlier for diphenylmethane is also valid for the present bisarene aromatic ligands containing hetero-atoms in their structures. Differing from the behaviour of the ^1H NMR chemical shifts of methylene protons of the diphenylmethane complexes, $\delta(^1\text{H})$ of $\text{Si}(\text{CH}_3)_2$ group in dimethyldiphenylsilane always shows deshielded values consistent with π -coordination. Similarly, $\delta(^{29}\text{Si})$ of $\text{Si}(\text{CH}_3)_2$ group is monotonously deshielded with the increasing degree of the complexation. As for diphenylmethane derivatives, $\delta(^{17}\text{O}\equiv\text{C})$ of the present chromium tricarbonyl derivatives always shows easy-to-detect spectral characteristics, the shifts varying between 372.8 and 374.5 ppm. The only value obtained for tetracobalt nonacarbonyl derivatives was that of 7, $\delta(^{17}\text{O}\equiv\text{C}) = 349$ ppm. The same order of $\delta(^{17}\text{O}\equiv\text{C})$ as observed for the mesitylene transition metal carbonyls ($\text{Co} < \text{Cr} < \text{Ru}$) is also valid for the present polyarene compounds. The inverse relation between $\delta(^{13}\text{C}\equiv\text{O})$ and $\delta(^{17}\text{O}\equiv\text{C})$ in Ru and Co derivatives can be explained by the effect of π -backbonding. Diphenylether derivatives were not thermally stable enough to determine accurately $\delta(^{17}\text{O})$ of the ethereal oxygen for all derivatives prepared. From the synthetic point of view, the present bisarene ligands were not so easily transformed to their π -coordinated derivatives as diphenylmethane.

Keywords: Chromium; Cobalt; Ruthenium; Nuclear magnetic resonance; Infrared spectroscopy

1. Introduction

Previously transition metal (Cr, W and Mn) arene tricarbonyls and transition metal (Ru and Co) carbonyl clusters have been characterized by NMR spectroscopy [1–4]. In addition to the ^{13}C NMR spectroscopic data, which have been collated exhaustively by Mann and Taylor [4], the ^{17}O NMR has often been shown to exhibit easy-to-detect spectral characteristics [1,3,5,6].

This finding prompted us to continue multinuclear magnetic resonance spectroscopic studies on aromatic transition metal carbonyls especially when a useful NMR nucleus, silicon-29 [7], is included in their structures. According to our previous experience diphenylmethane can be a suitable bifunctional ligand for preparing mono- and homo/heterobimetallic complexes with transition metal carbonyls [3]. In order to investigate further the properties of mono- and binuclear transition metal complexes and clusters as well as the influence of the ligand, the related bisarene compounds $\text{Ph}_2\text{Si}(\text{CH}_3)_2$, Ph_2O and Ph_2 have been selected for the present investigation.

[☆] Previous part, E. Kolehmainen et al., *J. Organomet. Chem.*, 485 (1995) 109.

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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 without precautions to exclude air and using standard solvents.

Ligand L1 (dimethyldiphenylsilane) was synthesized according to Benkeser and Foster [8]. Ligands L2 (diphenylether) and L3 (biphenyl) were analytical grade reagents and used without further purification.

(Dimethyldiphenylsilane tricarbonyl chromium, $(C_6H_5)_2Si(CH_3)_2Cr(CO)_3$) (**1**) and (dimethyldiphenylsilane hexacarbonyl dichromium, $(C_6H_5)_2Si(CH_3)_2[Cr(CO)_3]_2$) (**2**) were prepared according to the following procedure. A mixture of 0.60 g (3.2 mmol) of $(NH_3)_3Cr(CO)_3$ and 0.40 g (1.9 mmol) of Ph_2SiMe_2 was refluxed in 60 ml of dioxane for 6 h. After cooling the solvent was evaporated in vacuo. The residue was chromatographed on an Al_2O_3 column using a mixture of CH_2Cl_2 /petrol ether (with growing polarity) as eluent. Two yellow bands were first 170 mg of $Ph_2SiMe_2Cr(CO)_3$ (**1**) and secondly 64 mg of $Ph_2SiMe_2[Cr(CO)_3]_2$ (**2**). The complexes were recrystallized from hexane.

(Dimethyldiphenylsilane nonacarbonyltetracobalt, $(C_6H_5)_2Si(CH_3)_2Co_4(CO)_9$) (**3**) was synthesized by refluxing a mixture of 0.34 g (1.0 mmol) of $Co_2(CO)_8$ and 0.42 g (2.0 mmol) of Ph_2SiMe_2 in a solution of 50 ml of hexane and 25 ml of heptane for 24 h (in pure hexane the yield is lower, while in heptane total decomposition occurs). After cooling the reaction mixture was chromatographed on a SiO_2 column using mixture of CH_2Cl_2 /petrol ether (with growing polarity) as eluent. The second, green band gave 98 mg of **3**. The product was recrystallized from hexane.

(Dimethyldiphenylsilane octadecacarbonyl octacobalt, $(C_6H_5)_2Si(CH_3)_2[Co_4(CO)_9]_2$) (**4**) was obtained by refluxing a mixture of 140 mg (0.2 mmol) of **3** and

170 mg (0.50 mmol) of $Co_2(CO)_8$ in 80 ml of hexane for 24 h. After column chromatography, performed analogously as for **3**, two green bands were collected. The first gave 81 mg (58%) of the starting compound **3** and the second 29 mg (17%) of **4**.

(Dimethyldiphenylsilane tricarbonyl chromium nonacarbonyl tetracobalt, $(C_6H_5)_2Si(CH_3)_2Cr(CO)_3Co_4(CO)_9$) (**5**) was synthesized by refluxing 140 mg (0.40 mmol) of **1** and 300 mg (0.88 mmol) of $Co_2(CO)_8$ in 80 ml of hexane for 24 h. After work up, performed analogously to the previous case, the second, yellow band gave 119 mg (85%) of **1** and the third, green band gave 4.5 mg (1.3%) of **5**.

(Diphenylether tricarbonyl chromium, $(C_6H_5)_2OCr(CO)_3$) (**6**) was prepared according to the following procedure. A mixture of 0.50 g (2.3 mmol) of $Cr(CO)_6$ and 0.50 g (3.0 mmol) of Ph_2O was refluxed in a solution of 50 ml of diglyme and 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 mixture of CH_2Cl_2 /petrol ether (with growing polarity) as eluent. The only yellow band gave 167 mg of **6**, which was recrystallized from hexane.

(Diphenylether nonacarbonyl tetracobalt, $(C_6H_5)_2OCO_4(CO)_9$) (**7**) was obtained by refluxing 0.34 g (1.0 mmol) of $Co_2(CO)_8$ and 0.50 g (2.9 mmol) of Ph_2O in a solution of 50 ml of hexane and 25 ml of heptane for 30 h. After the usual work up the second, green band gave 52 mg of **7**. The complex was recrystallized from hexane.

(Diphenylether carbido tetradecacarbonyl hexaruthenium, $(C_6H_5)_2ORu_6C(CO)_{14}$) (**8**) was prepared according to the following procedure. A mixture of 0.30 g (0.47 mmol) of $Ru_3(CO)_{12}$ and 0.50 g (3.0 mmol) of Ph_2O was refluxed in 60 ml of octane for 14 h. After cooling the mixture was chromatographed on a SiO_2 column using a mixture of CH_2Cl_2 /petrol ether (with growing polarity) as eluent. The third, brown band gave 13.5 mg (5%) of **8**, which was recrystallized from CH_2Cl_2 /hexane mixture (v/v 1/10), m.p. 135–145°C

Table 1
Yields (%), melting points (°C) and elemental analyses (%) of compounds **1**, **2** and **3** (L1 = Ph_2SiMe_2) as well as **6** and **7** (L2 = Ph_2O)

Compound	Bruttoformula	Yield/%	Mp./°C	Analysis found/% (calc. %)				
				C	H	Cr	Co	Si
1 L1Cr(CO) ₃	C ₁₇ H ₁₆ CrO ₃ Si	26	56–59	58.82 (58.60)	4.98 (4.63)	14.64 (14.93)	–	7.76 (8.06)
2 L1[Cr(CO) ₃] ₂	C ₂₀ H ₁₆ Cr ₂ O ₆ Si	7	107–108 ^a	49.48 (49.58)	3.37 (3.33)	20.91 (21.47)	–	5.66 (5.80)
3 L1Co ₄ (CO) ₉	C ₂₃ H ₁₆ Co ₄ O ₉ Si	28	105–110 ^a	39.48 (39.45)	2.50 (2.30)	–	33.32 (33.67)	–
6 L2Cr(CO) ₃	C ₁₅ H ₁₀ CrO ₄	24	82–84	58.52 (58.83)	3.18 (3.29)	16.68 (16.98)	–	–
7 L2Co ₄ (CO) ₉	C ₂₁ H ₁₀ Co ₄ O ₁₀	16	112–114 ^a	38.65 (38.33)	1.58 (1.53)	–	35.79 (35.82)	–

^a With decomp.

Table 2
IR CO bands (cm^{-1}) of compounds 1–9. L1 = Ph_2SiMe_2 and L2 = Ph_2O

Compound	Solvent	
	Heptane	CH_2Cl_2
1 $\text{L1Cr}(\text{CO})_3$	1974, 1910	1964, 1884
2 $\text{L1}[\text{Cr}(\text{CO})_3]_2$	–	1964, 1891
3 $\text{L1Co}_4(\text{CO})_9$	2074m, 2027s, 2010m, 1996w, 1826m	–
4 $\text{L1}[\text{Co}_4(\text{CO})_9]_2$	2073m, 2026s, 2008m, 1995w, 1826m	–
5 $\text{L1Cr}(\text{CO})_3\text{Co}_4(\text{CO})_9$	2069m, 2024s, 2006m, 1993w, 1975w, 1906w, 1827w	–
6 $\text{L2Cr}(\text{CO})_3$	1975, 1908	1965, 1894
7 $\text{L2Co}_4(\text{CO})_9$	2071m, 2030s, 2011m, 1995w, 1825m	–
8 $\text{L2Ru}_6\text{C}(\text{CO})_{14}$	2072m, 2030s, sh, 2024vs, 2005w, 1982w, 1966m, 1906w, 1822w	–
9 $\text{L2Cr}(\text{CO})_3\text{Co}_4(\text{CO})_9$	2073w, 2030s, 2015m, 1989m, 1978s, 1920s, 1907s, 1823w	–

(with decomp.). Mass spectrum, $[m/e]^+$: 1183 (calc. 1181), $[\text{M} - \text{CO}]^+$, $[\text{M} - 2\text{CO}]^+$ etc.—successive loss of 14 carbonyl groups up to $[\text{M} - 14\text{CO}]^+ = 789$ was observed.

(Diphenylether tricarbonyl chromium nonacarbonyl tetracobalt, $(\text{C}_6\text{H}_5)_2\text{OCr}(\text{CO})_3\text{Co}_4(\text{CO})_9$ (**9**) unfortunately was obtained only as traces (yield < 1%) and could be characterized only by IR and ^1H NMR spectra.

The binuclear complex $(\text{C}_6\text{H}_5)_2\text{O}[\text{Cr}(\text{CO})_3]_2$ and bicluster $(\text{C}_6\text{H}_5)_2\text{O}[\text{Co}_4(\text{CO})_9]_2$ were not obtained at all.

(Biphenyl carbido tetradecacarbonyl hexaruthenium, $\text{Ph}_2\text{Ru}_6\text{C}(\text{CO})_{14}$ (**10**) was synthesized as described by Kaganovich et al. [9]. Mass spectrum, $[m/e]^+$: $[\text{M}]^+ = 1166$ (calc. 1166).

The melting points and results of the elemental analyses of the compounds prepared are collected in

Table 3
 ^1H , ^{17}O and ^{29}Si NMR of chromium, cobalt and ruthenium carbonyl complexes and clusters with dimethyldiphenylsilane (L1), diphenylether (L2) and diphenyl (L3) at 30°C in CDCl_3

Compound	$\delta(^1\text{H})^a/\text{ppm}$						$\text{Si}(\text{CH}_3)_2$	$\delta(^{17}\text{O})^b/\text{ppm}$			$\delta(^{29}\text{Si})^a/\text{ppm}$
	Noncoordinating ring			π -coordinating ring				CO	–O–		
	H-2/6	H-3/5	H-4	H-2/6	H-3/5	H-4					
L1	7.50	7.30	7.29	–	–	–	0.53	–	–	–8.02	
1 $\text{L1Cr}(\text{CO})_3$	7.57	7.40	7.40	5.38	5.11	5.50	0.59	372.8	–	–4.35	
2 $\text{L1}[\text{Cr}(\text{CO})_3]_2$	–	–	–	5.45	5.16	5.57	0.62	374.0	–	–0.99	
3 $\text{L1Co}_4(\text{CO})_9$	7.3 ^c	7.3 ^c	7.3 ^c	6.43	6.10	6.56	0.88	not obs.	–	–3.56	
4 $\text{L1}[\text{Co}_4(\text{CO})_9]_2$	–	–	–	6.15	6.02	6.53	1.17	not obs.	–	not obs.	
5 $\text{L1Cr}(\text{CO})_3\text{Co}_4(\text{CO})_9$	–	–	–	5.10	5.01	5.48 ^d	0.60	377.5	–	not obs.	
				6.48	6.17	6.63 ^e					
L2	7.00	7.13	7.09	–	–	–	–	–	115 ^f	–	
	–	–	–	–	–	–	–	–	115 ^g	–	
6 $\text{L2Cr}(\text{CO})_3$	7.18	7.42	7.25	5.11	5.50	4.86	–	373.8	not obs.	–	
	–	–	–	–	–	–	–	374.5	110.1 ^g	–	
7 $\text{L2Co}_4(\text{CO})_9$	7.05	7.41	7.24	6.05	6.16	5.84	–	349.1	not obs.	–	
$\text{L2Co}_4(\text{CO})_9^h$	7.05	7.42	7.27	6.10	6.21	5.89	–	not obs.	not obs.	–	
8 $\text{L2Ru}_6\text{C}(\text{CO})_{14}$	6.99	7.42	7.26	5.61	5.53	5.31	–	392.9	not obs.	–	
9 $\text{L2Cr}(\text{CO})_3\text{Co}_4(\text{CO})_9$	–	–	–	5.07	5.48	4.91 ^d	–	not obs.	not obs.	–	
				6.2	6.2	5.9 ^e					
L3 ⁱ	7.58	7.41	7.32	–	–	–	–	–	–	–	
10 $\text{L3Ru}_6\text{C}(\text{CO})_{14}$	7.42	7.31	7.25	5.92	5.72	5.56	–	not obs.	–	–	

^a From internal TMS.

^b From external H_2O .

^c Overlapping signals.

^d Cr-coordinated ring.

^e Co-coordinated ring.

^f Value taken from S. Chandrasekaran, in D.W. Boykin (ed.), *^{17}O NMR Spectroscopy in Organic Chemistry*, CRC Press, Boca Raton, Florida, 1991, p. 193.

^g Measured in CH_3CN at 75°C. $W_{1/2} > 1000$ Hz.

^h Measured in CD_2Cl_2 .

ⁱ Values taken from M. Yanagisawa, K. Hayamizu and O. Yamamoto, *Magn. Reson. Chem.*, 24 (1986) 1013.

Table 1. IR spectral $\nu(\text{C}\equiv\text{O})$ stretching bands are given in Table 2.

2.2. NMR Spectroscopy

^1H , ^{13}C , ^{17}O and ^{29}Si NMR spectra were recorded on a Jeol GSX 270 FT NMR spectrometer working at 270.17, 67.94, 36.63 and 53.54 MHz, respectively.

^1H NMR experiments were performed at 30°C in 5 mm diameter NMR tubes for saturated CDCl_3 solutions. The spectral width in ^1H experiments was 3500 Hz and the number of data points 32 000 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 ratio signal/noise (S/N) in the frequency spectra. All ^1H NMR chemical shifts are internally referenced to tetramethylsilane (TMS).

^{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 ratio signal/noise (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.

^{29}Si NMR experiments were performed at 30°C in 5 mm diameter NMR tubes for saturated CDCl_3 solutions using SGNNE pulse sequence in order to prevent the unfavourable influence of negative NOE [7]. The spectral width in ^{29}Si experiments was 10000 Hz and the number of data points 32000 giving a 1.2 Hz digital resolution. The acquisition time was 1.5 s, pulse delay 20 s, number of scans 500–1000 and flip angle 90° (18.0 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 ^{29}Si NMR chemical shifts are internally referenced to the signal of TMS.

3. Results and discussion

The IR CO bands, ^1H , ^{17}O , ^{29}Si and ^{13}C NMR chemical shifts of the compounds 1–10 are collected in Tables 2–4. The significant shielding effects of ^1H and ^{13}C NMR chemical shifts experienced by the π -coordi-

Table 4

^{13}C NMR chemical shifts of chromium, cobalt and ruthenium carbonyl complexes and clusters with dimethyldiphenylsilane (L1), diphenylether (L2) and biphenyl (L3) at 30°C in CDCl_3

Compound	$\delta(^{13}\text{C})^a/\text{ppm}$									
	Noncoordinated ring				π -coordinated ring					
	C-1	C-2/6	C-3/5	C-4	C-1	C-2/6	C-3/5	C-4	$(\text{CH}_3)_2$	CO
L1	138.20	134.16	127.80	129.07	–	–	–	–	–2.39	–
1 $\text{L1Cr}(\text{CO})_3$	135.88	134.07	128.14	129.88	97.95	99.94	90.26	95.61	–2.80	232.99
2 $\text{L1}[\text{Cr}(\text{CO})_3]_2$	–	–	–	–	94.89	99.57	90.11	95.96	–3.34	232.57
3 $\text{L1Co}_4(\text{CO})_9$	136.21	133.72	128.10	129.78	104.86	99.05	93.47	96.32	–3.39	210 ^b
4 $\text{L1}[\text{Co}_4(\text{CO})_9]_2$	–	–	–	–	102.37	98.56	93.46	96.70	–3.99	not obs.
5 $\text{L1Cr}(\text{CO})_3\text{Co}_4(\text{CO})_9$	–	–	–	–	94.48	99.50	89.63	95.97	–3.63	232.16
					104.70	98.72	93.58	96.87 ^c	–	–
L2	157.23	118.85	129.68	123.14	–	–	–	–	–	–
6 $\text{L2Cr}(\text{CO})_3$	152.99	121.22	130.29	126.00	not obs.	80.09	94.37	85.89	–	233.01
7 $\text{L2Co}_4(\text{CO})_9$	155.07	119.82	130.32	125.62	108.02	83.68	93.19	90.36	–	not obs.
8 $\text{L2Ru}_6\text{C}(\text{CO})_{14}$	not obs.	119.25	130.48	126.32	not obs.	80.74	84.81	84.81	–	202 ^b
9 $\text{L2Cr}(\text{CO})_3\text{Co}_4(\text{CO})_9$	not obs.	–	–	–	not obs.	–	–	–	–	–
L3 ^d	140.6	126.7	128.4	126.9	–	–	–	–	–	–
10 $\text{L3Ru}_6\text{C}(\text{CO})_{14}$	133.67	130.89	128.89	128.21	110.37	88.89	85.87	85.33	–	201.5

^a From internal TMS. ^b Broad signal $W_{1/2} > 200$ Hz. ^c Co-coordinated ring. ^d Values taken from E. Breitmaier and W. Voelter, *Carbon-13 NMR Spectroscopy, High-Resolution Methods and Applications in Organic Chemistry and Biochemistry*, Third, completely revised edition, VCH Verlagsgesellschaft mbH, Weinheim, 1987, p. 256.

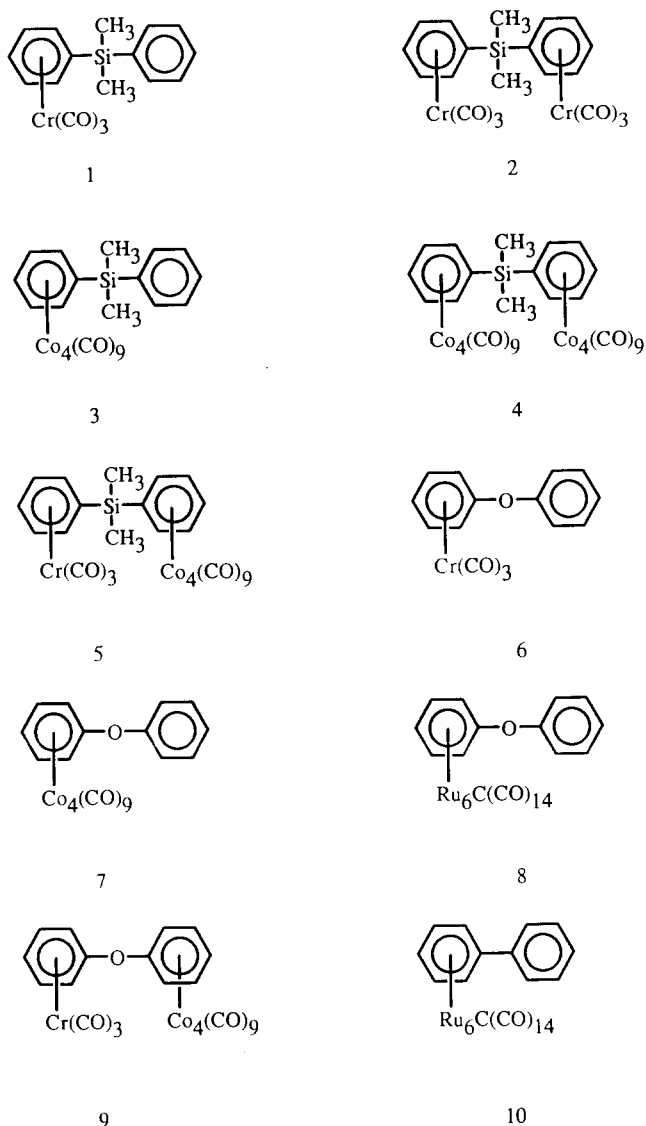


Fig. 1. Structures of compounds 1–10.

nated rings of all compounds studied and observed previously also for mesitylene (1,3,5-trimethylbenzene) [1] and diphenylmethane derivatives [3] can be explained by the diamagnetic screening of the metal valence electrons [10].

3.1. ^1H NMR

In diphenylmethane derivatives [3] the exocyclic methylene protons showed either shielded or deshielded values depending on the π -coordinated metal. Clearly deshielded shifts of diphenylmethane tetracobalt nonacarbonyl complexes were explained by the different conformational states adopted by the ligand in different solvents. The ^1H NMR chemical shifts of the $\text{Si}(\text{CH}_3)_2$ group of the dimethyldiphenylsilane derivatives do not exhibit that behaviour. Instead, all ^1H NMR chemical shifts of the $\text{Si}(\text{CH}_3)_2$ group are

deshielded up to 1.17 ppm (4) from the value of the ligand itself, 0.53 ppm. This is probably due to the steric hindrance between the exocyclic methyl groups and the transition metal moiety.

As in the case of diphenylmethane derivatives [3], the order of the shielding effects induced by the transition metal on the protons of the π -coordinated ring of dimethyldiphenylsilane and diphenylether derivatives is the same being $\text{Co} < \text{Ru} < \text{Cr}$. Consequently, a change of the central atom does not influence remarkably the strength of the π -coordination with a known transition metal carbonyl. However, the yields in the syntheses of bimetallic derivatives 2, 4, 5 and 9 are generally much lower than in those of diphenylmethane. This may be due to the steric hindrance of the bulky dimethylsilyl group when compared with the CH_2 moiety of diphenylmethane. In the case of diphenylether, the lone pairs of the central oxygen can also influence, by changing the π -electron distribution in the aryl rings, or directly due to a competing reaction with metal carbonyls leading to fast decomposition.

3.2. ^{13}C NMR

As in the case of ^1H and ^{13}C NMR chemical shifts of the mesitylene [1] and diphenylmethane derivatives [3], the ^{13}C NMR chemical shifts of the present compounds are strongly shielded with the π -coordination. In this case, however, the mutual variation of aryl carbons is larger than in diphenylmethane derivatives. For example, comparison of the compounds 1 and 3 reveals that the carbons 2/6 and carbon 4 differ less than 1 ppm in respect of their chemical shifts while carbons 1 and 3/5 show differences of ca. 7 and 3 ppm. In diphenylmethanetricarbonylchromium and nonacarbonyltetracobalt [3] these differences are remarkably smaller than in dimethyldiphenylsilane. This finding suggests that the π -system of the latter ligand is more easily polarizable than that of diphenylmethane. It is understandable that in diphenylether this phenomenon is still enhanced owing to the electron lone pairs of oxygen being available for conjugation with the π -system of the aromatic ring.

The ^{13}C NMR chemical shifts of carbonyl groups show metal-dependent variation in the order $\delta[\text{LRu}_6\text{C}(\text{CO})_{14}] < \delta[\text{LCo}_4(\text{CO})_9] < \delta[\text{LCr}(\text{CO})_3]$. In the case of tetracobalt nonacarbonyl only one broad signal was observed, at 30°C, owing to fast exchange of different carbonyl groups.

The dimethylsilyl moiety resonates upfield from TMS, the ^{13}C NMR chemical shifts varying from -2.39 in ligand itself to -3.99 in 4.

3.3. ^{17}O NMR

The ^{17}O NMR chemical shifts of carbonyl groups also show transition metal-dependent variation in the

order $\delta[\text{LCo}_4(\text{CO})_9] < \delta[\text{LCr}(\text{CO})_3] < \delta[\text{LRu}_6\text{C}(\text{CO})_{14}]$. The chemical shift order in comparison with the ^{13}C NMR chemical shifts is generally explained by the backdonation of the metal d-orbital to the π^* -orbital of CO [5]. Similarly as in ^{13}C NMR experiments, only single ^{17}O resonance lines were observed for cobalt and ruthenium derivatives suggesting fast exchange conditions between the various CO groups.

Unfortunately, diphenylether derivatives were not thermally stable enough to allow the ^{17}O NMR chemical shift determination of the ethereal oxygen at 75°C. That elevated temperature was necessary because at room temperature only very broad resonance line was observed owing to the unfavourable rotational correlation time of diphenylether oxygen. Only the compound **6** gave an observable signal, $\delta = 110$ ppm, differing 5 ppm from the shift of ligand itself under the same conditions.

3.4. ^{29}Si NMR

In the present series of compounds, silicon-29 provides a new angle on the topic of arene transition metal carbonyls comparable in sensitivity with that of carbon-13 [7]. The ^{29}Si NMR chemical shifts of mono- and bichromium derivatives **1** and **2** show monotonous deshielding with the π -coordination. The difference between the ligand itself and the monocoordinated complex is 3.67 ppm and between the bicoordinated and monocoordinated ones 3.66 ppm. This behaviour is very similar to the variation of the ^{13}C NMR chemical shift of the methylene carbon in diphenylmethane [3].

Although there exists a plethora of empirical correlations between ^{29}Si NMR chemical shifts and structural and electronic descriptors [7], the present data are too limited for any far reaching discussion. For example, the observed variation can be explained by changes in electronic interactions between d-orbitals of silicon and the aromatic π -system (bond order term of paramagnetic screening tensor) and/or by changed electronic charge on the silicon atom by complexation of transition metal.

3.5. ^{59}Co NMR

Unfortunately, neither the starting compound, dicobalt octacarbonyl, nor tetracobalt nonacarbonyl complexes gave ^{59}Co NMR lines sharp enough to be detected although the reference standard, 5% aqueous $\text{K}_3\text{Co}(\text{CN})_6$ -solution [11] gave a sharp and strong signal in this experiment. Thus it seems obvious that in structures containing Co–Co bonds, ^{59}Co NMR is often impractical owing to the broadness of resonance lines.

In the IR spectrum of complex **9** one can observe a splitting of the E-band, corresponding to vibration of the $\text{Cr}(\text{CO})_3$ group (1920, 1907 cm^{-1}), while in the

complex **6** this band is degenerate (1908 cm^{-1}). This fact suggests that the coordination of the second phenyl ring of diphenylether with the $\text{Co}_4(\text{CO})_9$ cluster introduces into the molecule a sufficient asymmetry with effects on the vibrations of the $\text{Cr}(\text{CO})_3$ group. Earlier such a phenomenon was observed only in analogous derivatives of biphenyl [9], while in the mixed complexes of diphenylmethane, $\text{Ph}_2\text{CH}_2\text{Cr}(\text{CO})_3\text{Co}_4(\text{CO})_9$ [12] and dimethyldiphenylsilane $\text{Ph}_2\text{SiMe}_2\text{Cr}(\text{CO})_3\text{Co}_4(\text{CO})_9$ (**5**) such an influence was not found. Apparently, the oxygen bridge can transmit that inter-ring effect better than carbon or silicon, being comparable with the direct bond between both coordinated rings as in the case of biphenyl.

4. Conclusions

NMR spectroscopy provides a variety of versatile methods for characterizing the arene transition metal carbonyls. In addition to the ^1H and ^{13}C NMR experiments, ^{17}O and ^{29}Si nuclei provide valuable means to probe the different parts of these complex structures. By comparing the present results of diphenyldimethylsilane complexes with those of diphenylmethane, one can suggest that diphenyldimethylsilane derivatives are conformationally more restricted than in diphenylmethane. This observation can be important from the point of view of catalytic activity and its control.

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