

Organometallic derivatives of the transition elements

IX *. Polynuclear π -complexes

Ted M. Pettijohn and J.J. Lagowski *

The University of Texas at Austin, Austin, Texas 78712 (U.S.A.)

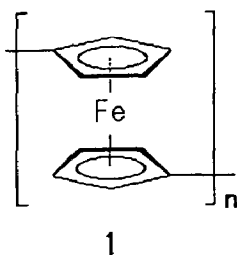
(Received April 1st, 1988)

Abstract

The synthesis and characterization of several mono- and di-substituted bis(di-arene)chromium-[tricarbonylchromium] complexes is described, where the diarene is a biphenyl-like ligand. A number of carbon based groups incorporating different hybridizations are used as spacers between the π -coordinated rings in the diarene moiety. The effect of the spacing group upon the inductive and resonance effects on electronic communication between metal sites in these systems is discussed using data from infrared and ^1H NMR spectroscopy.

Introduction

The properties of organometallic polymers containing π -bonded metal atoms in the backbone are potentially important from both academic and practical standpoints. Much of the work published thus far on such systems involve ferrocene-containing species **1** [1,2,3]. Relatively little information is presently available on the



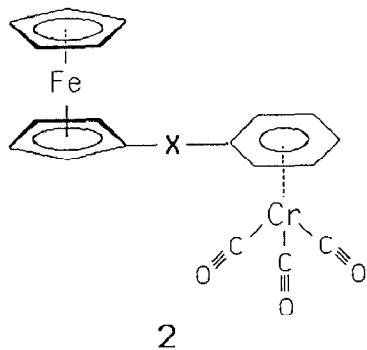
analogous arenechromium compounds [4,5,6].

Evidence is available [7] suggesting that electronic communication occurs between metal sites in disubstituted biphenyl- and stilbene-tricarbonylchromium com-

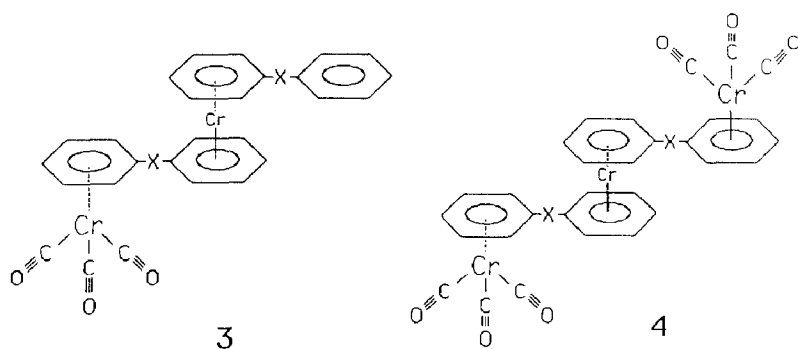
* For part VIII see ref. 1.

pounds. However, metal–metal communication is not observed in the corresponding diphenyldimethylstannane complexes [8].

Recently, reports on (phenyltricarbonylchromium)ferrocene complexes, **2**, provide a link between the ferrocene and the arenetricarbonylchromium studies [9,10]. In the complexes studied, the ferrocene unit is connected by a spacing group, X, to a phenyltricarbonylchromium moiety.



We have developed a viable general route for the synthesis of bis(polyarene)chromium(0) complexes [11], e.g., bis(biphenyl)chromium, which have two arene rings available for further π -coordination to other metal atoms. The availability of the bis(diarene)chromium complexes allows the synthesis of bis(diarene)chromium-[tricarbonylchromium] compounds of types **3** and **4**, where X = *trans*-CH=CH (**a**), none ($2e^-$, **b**), CH₂ (**c**) or CH₂CH₂ (**d**).



We report here the synthesis and characterization of several complexes of the types **3** and **4**. The diarene ligands, *trans*-stilbene (**a**), biphenyl (**b**), diphenylmethane (**c**), and bibenzyl (**d**), were chosen to vary the geometry and pathways for potential electronic interactions between the π -complexed metal sites.

The interactions between the metal sites in these environments were studied by infrared and ¹H NMR spectroscopy. Infrared analysis of the carbonyl stretching region yields information on the electron density at the Cr(CO)₃ site(s). The ¹H NMR spectrum of π -coordinated arenes is very sensitive to inductive and resonance electronic effects [18].

Experimental

All reagents were purchased from Aldrich and were of the highest purity available. Solid compounds were used without further purification. Liquids were dried by conventional methods and deoxygenated prior to use by passing dry argon through them for 20 min. All reactions were conducted under anaerobic conditions using standard techniques. The products obtained were also handled and stored under an inert atmosphere at all times. Melting points were obtained using an Electrothermal Melting Point Apparatus, the samples being contained in sealed, He-filled, capillaries and are reported as uncorrected.

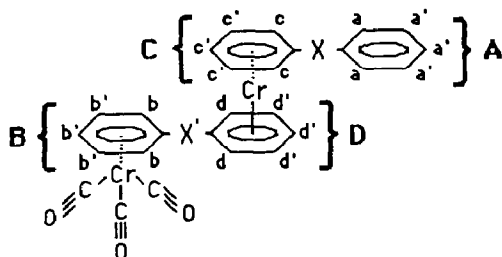
Analyses and characterization

All ^1H NMR spectra were recorded using a Varian EM-390 instrument; chemical shifts are referenced to internal Me_4Si (0.0 ppm δ). The ^1H NMR data for the compounds of types 3 and 4 are listed in Tables 1 and 2, respectively.

All infrared spectra, $\nu(\text{CO})$, were recorded as Nujol mulls between CsI plates using a Beckman A-8 spectrophotometer.

Table 1

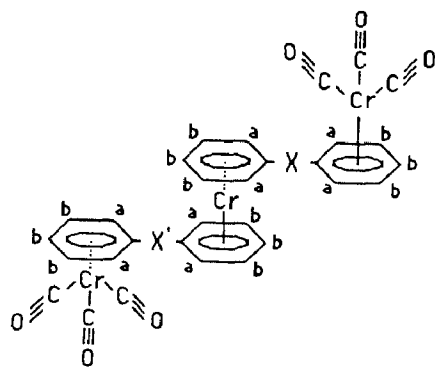
^1H NMR assignments of spectra of $(\text{diarene})_2\text{Cr}[\text{Cr}(\text{CO})_3]$, type 3 complexes



Diarene	Phenyl rings ^a				Spacing group X
	A	B	C	D	
<i>trans</i> -stilbene ^b	a, a' 6.89–7.86 (bm)	b, b' (c, c') 4.18–4.69 (bm)	c, c' (b, b') 4.18–4.69 (bm)	d, d' 3.15–3.66 (bm)	x 6.89–7.68 (bm) x' 4.81–4.93 (m), 2.63–2.72 (m)
Biphenyl ^b	a 7.43–7.52 (bm) a' 7.14–7.29 (bm)	b 5.66–5.73 (bm) b' 5.34–5.55 (bm)	c 4.78–4.99 (bm) c' 4.43–4.54 (bm)	d 3.43 (s) d' 3.26 5(s)	–
Diphenylmethane ^c	a, a' 7.12 (s)	b, b' 4.28–4.33 (m)	c, c' 4.12–4.28 (m)	d, d' 3.57 (m)	x, x' 3.79 (m)
Dibenzyl ^c	a, a' 7.16 (s)	b, b' (c, c'; d, d') 3.52–4.83 (bm)	c, c' (b, b'; d, d') 3.52–4.83 (bm)	d, d' (b, b'; c, c') 3.52–4.83 (bm)	x, x' 2.46–2.91 (m)

^a Shifts are reported in ppm δ from Me_4Si (0.0 ppm δ). ^b Solvent CD_3CN . ^c Solvent C_6D_6 .

Table 2

¹H NMR assignments of spectra of (diarene)₂Cr[Cr(CO)₃]₂, type 4 complexes

Diarene ^b	Chemical shift ^a		
	a	b	x
<i>trans</i> -Stilbene	3.40–3.49 (m)	3.21 (s)	3.37 (s)
Biphenyl	3.32 (s)	3.52 (s)	–
Diphenylmethane	3.43–3.50 (m)	3.25 (s)	3.41 (s)
Bibenzyl	3.44 (s)	3.28 (s)	2.03–2.12 (m)

^a In ppm δ from Me₄Si (0.0 ppm δ). ^b Solvent CD₃CN.

Chemical ionization mass spectra (CIMS) were obtained using a Finnigan-MAT 4023 quadrupole mass spectrometer utilizing an INCOS data system. Methane was used as the reagent gas at an ion source pressure of 0.5 torr. Samples were introduced into the ionizer with a solid probe from capillary tubes that had been prepared in a He atmosphere dry box. Characteristic chromium isotope patterns were observed in metal-containing fragments. Exact mass measurements were made by high resolution mass spectrometry (HRMS) using a Consolidated Electro-dynamics Model 21-110B spectrometer with 15 to 20,000 (70 eV) resolution.

Syntheses

The bis(diarene)chromium compounds were prepared using conventional metal-atom synthesis techniques described previously [11].

Bis(η^6 -bibenzyl)chromium. Chromium metal (490 mg, 9.42×10^{-3} mol) was evaporated into bibenzyl (9.4 g, 5.2×10^{-2} mol) using a time-averaged power of 380 W at an average pressure of 4.6×10^{-6} torr over a period of 0.5 h. After purification by sublimation, bis(bibenzyl)chromium (609 mg, 1.46×10^{-3} mol, 16% yield (based on the metal evaporated)) was collected: m.p. 100–103°C, exact mass C₂₈H₂₈Cr, calcd. 416.15959, measd. 416.16232, error 2.7 mAMU/6.6 ppm.

The synthesis and characterization of the other bis(diarene)chromium complexes is described elsewhere [11]. ¹H NMR data is provided (vide infra) for reference purposes.

(Diarene)tricarbonylchromium complexes. These compounds were prepared from the diarene and either Cr(CO)₆ or (MeCN)₃Cr(CO)₃ using previously described

procedures [12,13,14]. The infrared and ^1H NMR data are provided for reference purposes.

The purity and identity of the bis(diarene)chromium compounds and the corresponding arenetricarbonyl complexes were determined from their melting points, ^1H NMR spectra, and high resolution mass spectral measurements.

Complexes of type **3** and **4** were prepared by refluxing the corresponding bis(diarene)chromium compound with excess $(\text{MeCN})_3\text{Cr}(\text{CO})_3$ in THF. Samples of $(\text{MeCN})_3\text{Cr}(\text{CO})_3$ were prepared by refluxing $\text{Cr}(\text{CO})_6$ in acetonitrile [15].

(η^6 -trans-stilbene) [η^6 -(η^6 -trans-stilbenetricarbonylchromium)]-chromium (**3a**), and *bis* [η^6 -(η^6 -trans-stilbenetricarbonylchromium)]chromium (**4a**). Bis(*trans*-stilbene) chromium (239 mg, 5.80×10^{-4} mol) and $(\text{MeCN})_3\text{Cr}(\text{CO})_3$ (1.132 g, 4.37×10^{-3} mol) were refluxed in 15 ml THF for 2 h at 55°C . The products were isolated by column chromatography (celite). Elution of the column with hexanes developed a burgundy band. Solvent removal in vacuo from this fraction produced a burgundy solid, **3a**, (77 mg, 1.41×10^{-4} mol, 24% yield): m.p. $161\text{--}163^\circ\text{C}$; IR: ($\nu(\text{CO})$) 1965(s), 1898 (w, br) cm^{-1} , CIMS: m/z (relative intensity) 549 (0.3, M^+ (+H)), 412(35.0), 317(6.2), 261(3.1), 233(18.2), 181(100); exact mass $\text{C}_{31}\text{H}_{24}\text{Cr}_2\text{O}_3$, calcd. 548.053555, measd. 548.054664, error 1.09 mAMU/1.99 ppm.

Further elution of the column with glyme produced an intense red-brown fraction. Solvent removal from this fraction yielded a red-brown solid, **4a** (294 mg, 4.30×10^{-4} mol, 74% yield): m.p. 239°C (dec.); IR: ($\nu(\text{CO})$) 1983(s), 1885(w, br) cm^{-1} ; CIMS: m/z (relative intensity), 600 (0.9, M^+ [-3CO]), 548(0.6), 464(0.3), 412(37.2), 284(2.0), 261(1.6), 233(11.1), 181(100); exact mass $\text{C}_{28}\text{H}_{24}\text{Cr}$, calcd. 412.128301, measd. 412.128948, error 0.44 mAMU/1.57 ppm; $\text{C}_{17}\text{H}_{12}\text{CrO}_3$ calcd. 316.019148, measd. 316.019666, error 0.52 mAMU/1.64 ppm.

Black insoluble decomposition products remained on top of the column.

(η^6 -Biphenyl) [η^6 -(η^6 -biphenyltricarbonylchromium)]chromium (**3b**), and *bis* [η^6 -(η^6 -biphenyltricarbonylchromium)]chromium (**4b**). Bis(biphenyl)chromium (207 mg, 5.75×10^{-4} mol) and $(\text{MeCN})_3\text{Cr}(\text{CO})_3$ (740 mg, 2.86×10^{-3} mol) were refluxed in 10 ml THF for 5 h at 55°C . The products were isolated by column chromatography (celite). Unreacted bis(biphenyl)chromium eluted with hexanes. Elution with a 1/1 mixture of hexanes and cyclohexane produced an orange-brown fraction. After solvent removal, a brown solid **3b** was obtained from this fraction (156 mg, 2.95×10^{-4} mol, 51%): m.p. $108\text{--}111^\circ\text{C}$; IR: ($\nu(\text{CO})$) 1978(s), 1939(w, br) cm^{-1} ; CIMS: m/z (relative intensity), 496 (5.1, M^+) 469(19.0), 412(5.0), 360(59.1), 155(100); exact mass $\text{C}_{27}\text{H}_{20}\text{Cr}_2\text{O}_3$, calcd. 496.022256, measd. 496.022604, error 0.35 mAMU/0.70 ppm.

Further elution of the column with glyme developed a red-brown fraction. Removal of solvent left a black-brown solid, **4b** (22 mg, 3.48×10^{-5} mol, 6.1% yield): m.p. $324\text{--}326^\circ\text{C}$ (dec.); IR: ($\nu(\text{CO})$) 1982(s), 1935(w, br) cm^{-1} ; CIMS: m/z (relative intensity), 576[0.6, $M^+ - 2\text{CO}$], 548(2.3), 520(2.7), 492(0.6), 496(4.8), 412(6.4), 360(100), 155(35.0); exact mass $\text{C}_{24}\text{H}_{20}\text{Cr}$, calcd. 360.097003, measd. 360.097711, error 0.71 mAMU/1.97 ppm; $\text{C}_{15}\text{H}_{10}\text{CrO}_3$, calcd. 290.003499, measd. 290.003964, error 0.46 mAMU/1.60 ppm.

Black insoluble decomposition products remained on top of the column.

(η^6 -Diphenylmethane) [η^6 -(η^6 -diphenylmethanetricarbonylchromium)]chromium (**3c**), and *bis* [η^6 -(η^6 -diphenylmethanetricarbonylchromium)]chromium (**4c**). Bis(diphenylmethane)chromium (510 mg, 1.31×10^{-3} mol) and $(\text{MeCN})_3\text{Cr}(\text{CO})_3$ (959 mg,

3.70×10^{-3} mol) were refluxed in 7.5 ml THF and 7.5 ml hexanes for 2 h at 55°C . The products were isolated by column chromatography (celite). Elution with hexanes developed a yellow-brown fraction. After solvent removal, a yellow-brown solid, **3c**, was collected 9442 mg, 8.44×10^{-4} mol, 64% yield): m.p. $118\text{--}119^\circ\text{C}$; IR: $\nu(\text{CO})$ 1988(s), 1963(vw), 1908(w), 1857(vw) cm^{-1} ; CIMS: m/z (relative intensity), 524(62, M^+), 388(28), 357(12), 329(100), 305(24), 298(10), 273(5.1), 221(16), 168(3.4), 91(39); exact mass $\text{C}_{29}\text{H}_{24}\text{Cr}_2\text{O}_3$, calcd. 524.053555, measd. 524.054765, error 1.21 m/AMU/2.31 ppm.

Further elution of the column with glyme produced a greenish-brown fraction. Solvent removal left a green-black solid **4c** (187 mg, 2.83×10^{-4} mol, 22%): m.p. 105°C (dec.); IR: ($\nu(\text{CO})$) 1973(s), 1936(w), 1911(vw) cm^{-1} ; CIMS: m/z (relative intensity), 388 [72, $M^+(-2\text{Cr}(\text{CO})_3)$], 305(21), 298(12), 221(8.3), 207(1.2), 131(3.0), 91(100); exact measd. $\text{C}_{26}\text{H}_{24}\text{Cr}$ calcd. 388.128301, measd. 388.128516, error 0.21 mAMU/0.55 ppm; $\text{C}_{16}\text{H}_{12}\text{CrO}_3$ calcd. 304.019148, measd. 304.019369, error 0.22 mAMU/073 ppm.

Black insoluble decomposition products remained on top of the column.

(η^6 -Bibenzyl)[η^6 -(η^6 -bibenzyltricarbonylchromium)]chromium (**3d**), and bis[η^6 -(η^6 -bibenzyltricarbonylchromium)]chromium (**4d**). Bis(bibenzyl)chromium (359 mg, 8.63×10^{-4} mol) and $(\text{MeCN})_3\text{Cr}(\text{CO})_3$ (739 mg, 2.85×10^{-3} mol) were refluxed in 15 ml THF for 2 h at 55°C . The products were isolated by column chromatography (celite). Elution with hexanes developed a yellow-brown fraction. After solvent removal, a yellow-brown solid, **3d**, was collected (281 mg, 5.09×10^{-4} mol, 59%): m.p. $102\text{--}105^\circ\text{C}$; IR: ($\nu(\text{CO})$) 1993(s), 1979(vw), 1955(w), 1914(vw); CIMS: m/z (relative intensity), 552(5.0, M^+), 416(100), 319(23), 287(3.1), 235(49), 221(5.3), 183(24), 105(88); exact mass $\text{C}_{31}\text{H}_{28}\text{Cr}_2\text{O}_3$ calcd. 552.084853, measd. 552.085628, error 0.77 mAMU/1.40 ppm.

Further elution with glyme produced a greenish-brown fraction. Solvent removal left the greenish-black solid, **4d**, (150 mg, 2.18×10^{-4} mol, 25% yield): m.p. 88°C (dec.); IR: ($\nu(\text{CO})$) 1982(s), 1950(vw), 1885(w, br) cm^{-1} ; CIMS: m/z (relative intensity) 416(63, $M^+[-2\text{Cr}(\text{CO})_3]$), 319(16), 235(28), 221(22), 183(37), 105(100); exact mass $\text{C}_{31}\text{H}_{28}\text{Cr}_3\text{O}_3$ calcd. 604.025364, measd. 604.025639, error 0.27 mAMU/0.45 ppm.

Black insoluble decomposition products remained on top of the column.

Reference data

^1H NMR data for bis(diarene)chromium complexes. All spectra were recorded in C_6D_6 ; chemical shifts are given in ppm, δ .

Bis(*trans*-stilbene)chromium: coord. ring 4.20 (6H, m), 4.53(4H, m); spacing group 6.68 (2H, s), 6.73 (2H, s); uncoord. ring 7.10 (10H, m). Bis(biphenyl)chromium: coord. ring 4.30 (6H, m), 4.81 (4H, m); uncoord. ring 7.21 (6H, m), 7.50 (4H, m).

Bis(diphenylmethane)chromium: coord. ring and spacing group 3.39–3.74 (14H, b m); uncoord. ring 7.41 (10H, s). Bis(bibenzyl)chromium: spacing group 2.69 (8H, b m); coord. ring 4.21 (10H, s); uncoord. ring 7.17 (10H, s).

IR and ^1H NMR (ppm δ) data for diarenetricarbonylchromium complexes. ^1H NMR chemical shifts are indicated in ppm, δ . Infrared spectra were recorded as a mull (Nujol) between CsI plates; only the frequencies in the carbonyl region are reported.

(*trans*-Stilbene)tricarbonylchromium: IR: 1971(s), 1899(s) cm^{-1} ; ^1H NMR (in CDCl_3): coord. ring 5.46 (5H, m), spacing group 6.82 (2H, quartet (J 15 Hz), uncoord. ring 7.48 (5H, m).

(Biphenyl)tricarbonylchromium. IR: 1968(s), 1902(s) cm^{-1} ; ^1H NMR (in CD_3COCD_3) coord. ring 5.69 (3H, m) 6.04 (2H, m), uncoord. ring. 7.42 (3H, m) 7.65 (2H, m). (Diphenylmethane)tricarbonylchromium. IR: 1970(s), 1900(s) cm^{-1} ; ^1H NMR (in CD_3COCD_3) spacing group 3.77 (2H, s), coord. ring 5.56 (5H, m), uncoord. ring 7.31 (5H, m).

(Bibenzyl)tricarbonylchromium. IR: 1977(s), 1909(s) cm^{-1} ; ^1H NMR (in CDCl_3): spacing group 2.79 (4H, m), coord. ring 5.22 (5H, m), uncoord. ring 7.27 (5H, m).

Results and discussion

The reaction of bis(diarene)chromium complexes and excess $(\text{MeCN})_3\text{Cr}(\text{CO})_3$ produces both the mono- (**3a–3d**) and di-substituted (**4a–4d**) chromiumtricarbonyl derivatives. Preliminary experiments suggest that the distribution of products does not appear to be a sensitive function of the amount of $(\text{MeCN})_3\text{Cr}(\text{CO})_3$ however, we are not able to make a statement on this point with the data available. All of the complexes are air and moisture sensitive reacting much like the parent bis(diarene)chromium compounds. Upon exposure to the atmosphere, type **4** complexes are especially reactive. They rapidly oxidize to the characteristic chromium(III) green color producing clear crystals of $\text{Cr}(\text{CO})_6$ in the process. The type **4** complexes are also thermally unstable; extensive decomposition occurs at or before melting.

The thermal instability of the compounds makes normal electron impact (EI) mass spectrometry difficult, although not impossible. The milder chemical ionization (CI) techniques produce M^+ for the type **3** complexes and ion fragments as large as $M^+ (-2\text{CO})$ for the type **4** compounds. The CI mass spectra for all type **3** and type **4** complexes indicate extensive fragmentation. However, characteristic chromium isotope patterns are observed in the metal-containing fragments which assists in the interpretation of the mass spectra of these compounds. Type **3** complexes are sufficiently stable in the vapor phase to allow exact mass measurements on the molecule ion using high resolution (EI) mass spectrometry. Exact mass measurements were made on ion fragments for the thermally unstable type **4** complexes. Care was taken to insure that the ions appear concurrently indicating that they are a result of parent ion decomposition and do not occur independently.

Infrared spectra

The A_1 and E carbonyl stretching modes in arenetricarbonylchromium complexes, are known to be sensitive to changes in electron density at the metal site arising from the nature of the ring substituents [16]. As electron density decreases at the metal site, back-bonding to the carbonyl groups also decreases, which results in an increase in the $\nu(\text{CO})$ frequencies. When the substituent is an electron donor, the opposite effect is found.

In general, comparison of the $\nu(\text{CO})$ frequencies in the complexes of types **3** and **4** with the corresponding uncomplexed diarenetricarbonylchromium compounds shows that the stretching frequencies shift to higher values, indicating a decrease in the electron density at the metal site. Thus, the bis(arene)metal moiety acts as an electron-withdrawing substituent in all complexes described here.

The carbonyl stretching frequencies decrease from the type **3** complexes to lower values in the type **4** compounds when the spacing group, X, is electronically insulating e.g., diphenylmethane and bibenzyl complexes, suggesting that electronic induction through the framework of the molecule is effectively blocked. The opposite effect is observed when the coordinated rings are potentially electronically interacting as in the case of *trans*-stilbene and biphenyl. Complexes which have spacers that can participate in electronic communication (e.g. through resonance effects) are much better equipped to accommodate partial negative charge [7] making the inductive effects of the Cr(CO)₃ moieties additive in nature.

The degenerate *E* mode broadens and even splits in some cases (e.g. diphenylmethane and bibenzyl complexes) indicating that the localized C_{3v} symmetry is disrupted to steric and/or electronic factors [17]. Our interpretations regarding the shifts of the carbonyl stretching frequencies are, therefore, based primarily upon the A₁ band and not the *E*.

¹H NMR spectra

Coordination of an arene to a metal causes a large upfield shift of the ring hydrogen atoms. In bis(arene)chromium [18] and arenetricarbonylchromium [19,20] complexes, the shift is attributed to a combination of inductive and resonance effects on metal–ligand bond anisotropy, on the quenching of ring currents, on changes in carbon atom hybridization and/or on electron density changes. In our complexes, the two metal systems are electronically linked and the effect on the shift is dramatic.

The ¹H NMR data for complexes to type **3** are listed in Table 1. The assignments are based upon the spectra of the corresponding bis(diarene) and diarenetricarbonyl complexes. The most obvious feature common to all of the spectra is an increased upfield shift of the resonance assigned to the coordinated ring hydrogen atoms. The upfield shift is approximately 1 ppm δ for the ring protons on the di-substituted diarene while the shift of the other diarene protons is much less. The increased shift observed for the disubstituted diarene must be attributed primarily to inductive rather than resonance effects because the same shift appears for all of the complexes reported here. No major dependence upon the degree of conjugation between the rings is detectable. The vinyl protons on the bridging ligand in **3a** are also shielded, however, indicating that resonance effects are possible.

Table 2 lists the ¹H NMR data and assignments for the type **4** compounds. The spectra of these disubstituted complexes contain two peaks that are assigned to the protons of the coordinated rings indicating that strong inductive effects are present that are independent of the individual spacing group. The two ring resonances integrate to a ratio of 2/3. Based upon that integration the peaks are assigned to the *ortho* and to the *meta* and *para* protons on each ring, respectively. The phenyl rings appear equivalent; however, it may be that their differences have not been resolved. Here, as with the type **3** complexes, induction appears to be the primary factor for the upfield shift since no major relationship among compounds incorporating different spacing groups seems to be present from the data available.

A common non-interfering solvent could not be found for the entire series of compounds; therefore, no quantitative conclusion based upon the changes in chemical shift is attempted here.

Preliminary observations on the electrochemical oxidation of the type-**3** and

type-4 complexes indicate a non-reversible oxidation of the chromium atoms at the tricarbonyl sites. However, the chromium atoms at the bis(π -arene) sites appear to undergo a reversible redox process. The details of these electrochemical studies will be presented elsewhere in context with our observations on the electrochemistry of a series of systematically substituted arenechromium π complexes.

Conclusion

The complexes of types 3 and 4 were prepared by treating $(\text{MeCN})_3\text{Cr}(\text{CO})_3$ with a bis(diarene)metal compound. Analysis of these new complexes indicated that resonance interaction between the coordinated arenes is much less important than the physical distance separating the active sites.

In the study described here, there is no system in which the metal sites are rigidly separated so as to preclude intramolecular interactions. We, therefore, plan to continue the study of these oligomeric systems using other spacing groups as well as other transition metals in the hope of gaining further insight into the physicochemical properties of the corresponding (larger) polymers.

Acknowledgement

We thank the Robert A. Welch Foundation and the Texas Advanced Technology Research Program for generous financial support.

References

- 1 Part VIII: B.F. Bush, V.M. Lynch, J.J. Lagowski, *Organometallics*, 6 (1987) 1267.
- 2 D.O. Cowan, C. Le Vanda, J. Park, F. Kaufman, *Acc. Chem. Res.*, 6 (1973) 1.
- 3 W.E. Geiger, N.G. Connelly, *Adv. Organomet. Chem.*, 24 (1986) 87.
- 4 L.P. Yureva, S.M. Perehudova, L.N. Nekrasov, A.P. Korotkov, N.N. Zaitseva, N.V. Zakurin, A.Yu. Vasilkov, *J. Organomet. Chem.*, 219 (1981) 43.
- 5 C. Elschenbroich, J. Heck, *J. Am. Chem. Soc.*, 101 (1979) 6773.
- 6 C. Elschenbroich, J. Heck, *J. Am. Chem., Int. Ed. Engl.*, 20 (1981) 267.
- 7 S.N. Milligan, R.D. Rieke, *Organometallics*, 2 (1983) 171.
- 8 R.D. Rieke, I. Tucker, S.N. Milligan, D.R. Wright, B.R. Willeford, L.J. Radonovich, M.W. Eyring, *Organometallics*, 1 (1982) 938.
- 9 S.P. Gubin, V.S. Khandkarova, *J. Organomet. Chem.*, 22 (1970) 449.
- 10 C. Degrand, J. Besancon, A. Radecki-Sudre, *J. Electroanal. Chem.*, 160 (1984) 199.
- 11 R.J. Markle, T.M. Pettijohn, J.J. Lagowski, *Organometallics*, 4 (1985) 1529.
- 12 B. Nicholls, M.C. Whiting, *J. Chem. Soc.*, (1959) 551.
- 13 S. Top, G. Jaouen, *J. Organomet. Chem.*, 182 (1979) 381.
- 14 R.B. King, *J. Organomet. Chem.*, 8 (1967) 139.
- 15 D.P. Tate, W.R. Knipple, J.M. Augl, *Inorg. Chem.*, 1 (1962) 433.
- 16 M. Herberhold, C.R. Jablonski, *Inorg. Chim. Acta*, 7 (1973) 241.
- 17 F. van Meurs, J.M.A. Baas, H. van Bekkum, *J. Organomet. Chem.*, 113 (1976) 353.
- 18 V. Graves, J.J. Lagowski, *J. Organomet. Chem.*, 120 (1976) 397.
- 19 T.K. Wu, B.P. Dailey, *J. Chem. Phys.*, 41 (1964) 2796.
- 20 H. Spiesscke, W.G. Schneider, *J. Chem. Phys.*, 35 (1961) 731.