Organometallics 1992, *11*, 1210–1220

$\{\eta^6$-(Organosilyl)arene$\}$chromium Tricarbonyl Complexes: Synthesis, Characterization, and Electrochemistry

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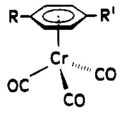
Received August 22, 1991

The synthesis of the complexes $\{\eta^6\text{-}C_6H_5Si(OEt)_3\}Cr(CO)_3$ (**1**), $\{\eta^6\text{-}C_6H_5SiMe(OMe)_2\}Cr(CO)_3$ (**2**), $\{\eta^6\text{-}C_6H_5(CH_2)_2Si(OMe)_3\}Cr(CO)_3$ (**3**), $\{\eta^6\text{-}1,4\text{-}C_6H_4[(CH_2)_2Si(OMe)_3]_2\}Cr(CO)_3$ (**4**), $\{\eta^6\text{-}C_6H_5Si(Me)_2H\}Cr(CO)_3$ (**5**), $\{\eta^6\text{-}1,4\text{-}C_6H_4[Si(Me)_2H]_2\}Cr(CO)_3$ (**6**), $\{\eta^6\text{-}C_6H_5Si(Me)_2CH{=}CH_2\}Cr(CO)_3$ (**7**), and $\{\eta^6\text{-}C_6H_5SiMe(NMe_2)_2\}Cr(CO)_3$ (**8**) is described. The compounds have been prepared by direct thermal reaction of the (organosilanyl)arene either with $Cr(CO)_6$ (in refluxing dibutyl ether–tetrahydrofuran (THF) solution) or from the acetonitrile complex $(MeCN)_3Cr(CO)_3$ in cyclohexane. Alternatively, some of these complexes can be obtained by reaction of the (η^6-lithiobenzene)- or (η^6-1,4-dilithiobenzene)$Cr(CO)_3$ derivatives with the appropriate chlorosilane, in THF at low temperature. Photochemical reactions of these tricarbonyl complexes with tri-*n*-butyl phosphite, in cyclohexane at room temperature, afford the corresponding dicarbonyl-monosubstituted $\{\eta^6$-(organosilyl)arene$\}Cr(CO)_2(P(OBu_3))$ complexes **9**–**16**. The (alkoxysilyl)arene derivatives **1**–**4** have been covalently linked to silica supports. New $\{$(siloxanyl)arene$\}Cr(CO)_3$ polymers $[-SiMe\{\eta^6\text{-}C_6H_5\}Cr(CO)_3OSiMe_2(1,4\text{-}C_6H_4)SiMe_2O-]_n$ (**17**), $[-CH_2CH\{\eta^6\text{-}C_6H_5SiMe_2\}Cr(CO)_3-]_n$ (**18**), and $[-SiMe_2\{\eta^6\text{-}1,4\text{-}C_6H_4\}Cr(CO)_3SiMe_2(CH_2)_2SiMe_2OSi(CH_2)_2-]_n$ (**19**) as well as the dinuclear model compound $\{\eta^6\text{-}C_6H_5SiMe_2(CH_2)_2SiMe_2-\}_2O[Cr(CO)_3]_2$ (**20**) have been prepared either by condensation or addition polymerization reactions from the monomers with the reactive $Si(NMe_2)_2$, $SiCH{=}CH_2$, and SiH groups. The oxidation of the $\{\eta^6$-(organosilyl)arene$\}Cr(CO)_3$ complexes has been studied by means of electrochemical and spectroelectrochemical (IR and EPR) techniques. The results show that the stability of the oxidation products is very dependent upon the solvent and ring substituents. An electrochemically induced process exhibiting curve crossing was observed when the oxidation was effected in the presence of $P(OBu)_3$ in dichloromethane or propylene carbonate. Chemical modification of platinum electrodes via silanization has been studied with the alkoxysilane complexes **1**–**4**.

Introduction

Transition-metal complexes containing π-bound arene rings have been extensively investigated because of both fundamental interest in the rich structural, stereochemical, and electronic features of metal–arene interactions and their utility in organic synthesis.[1-4] The $\{\eta^6$-arene$\}Cr(CO)_3$ complexes have been the most widely studied of such species because they are relatively air and thermally stable, they are reactive toward a wide variety of organic reagents, and for some arenes they are easily prepared. These compounds have been studied in a variety of applications, ranging from their use as stoichiometric asymmetric reagents, to models for ligand substitution reactions, being also efficient catalysts in several processes.[4]

Chart I



1 R = H R' = $Si(OEt)_3$
2 R = H R' = $SiMe(OMe)_2$
3 R = H R' = $(CH_2)_2Si(OMe)_3$
4 R = R' = $(CH_2)_2Si(OMe)_3$
5 R = H R' = $SiMe_2H$
6 R = R' = $SiMe_2H$
7 R = H R' = $SiMe_2CH{=}CH_2$
8 R = H R' = $SiMe(NMe_2)_2$

Our interest in $\{\eta^6$-arene$\}Cr(CO)_3$ complexes stems from our investigations into the synthesis of organometallic compounds containing organosilane groups. In the last several years we began a research with the goal of synthesizing new types of organometallic polymers derived of metal–cyclopentadienyls and metal–arenes, from monomers with alkoxysilanes, siloxanes (linear or cyclic), and some other organosilanes which contain easily polymerizable groups. In this way, we have previously reported the synthesis of some iron dinuclear complexes containing alkoxysilane- and siloxane-functionalized cyclopentadienyl ligands.[5,6] In addition, some iron and nickel complexes in which the alkoxysilane group is directly bound to the

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Table I. Analytical and Selected Spectroscopic Data for the $\{\eta^6$-(Organosilyl)arene$\}$chromium Tricarbonyl Complexes

	elemental anal., %: calcd (found)		IR data: ν(CO), cm^{-1} (CH_2Cl_2 soln)			^{1}H NMR data^a	
complex	C	H	A_1	E	(A_1 + 2E)/3	C_6H_5/C_6H_4	R/R′
$\{\eta^6$-$C_6H_5Si(OEt)_3\}Cr(CO)_3$ (**1**)	47.87 (47.75)	5.18 (5.30)	1971 (1977)^b	1895 (1906)^b	1921	5.12 (t, 2 H, H_m), 5.51 (t, H, H_p), 5.56 (d, 2 H, H_o)	1.28 (t, 9 H, CH_3), 3.93 (c, 6 H, OCH_2)
$\{\eta^6$-$C_6H_5SiMe(OMe)_2\}$-$Cr(CO)_3$ (**2**)	45.24 (45.47)	4.39 (4.48)	1971 (1976)^b	1892 (1902)^b	1918	5.14 (t, 2 H, H_m), 5.50 (t, H, H_p), 5.54 (d, 2 H, H_o)	0.41 (s, 3 H, CH_3), 3.61 (s, 6 H, OCH_3)
$\{\eta^6$-$C_6H_5(CH_2)_2Si(OMe)_3\}$-$Cr(CO)_3$ (**3**)	46.38 (46.22)	4.96 (5.13)	1965 (1970)^b	1886 (1896)^b	1912	5.23 (m, 3 H, $H_{o,p}$), 5.39 (t, 2 H, H_m)	0.95 (q, 2 H, CH_2Si), 2.50 (q, 2 H, CH_2C), 3.58 (s, 9 H, CH_3O)
$\{\eta^6$-1,4-$C_6H_4[(CH_2)_2Si$-$(OMe)_3]_2\}Cr(CO)_3$ (**4**)	44.66 (44.90)	5.87 (5.80)	1962 (1968)^b	1883 (1891)^b	1908	5.27 (s, 4 H, $H_{o,m}$)	0.93 (m, 4 H, CH_2Si), 2.47 (m, 4 H, CH_2C), 3.53 (s, 18 H, OCH_3)
$\{\eta^6$-$C_6H_5Si(Me)_2H\}$-$Cr(CO)_3{}^c$ (**5**)	48.47 (48.32)	4.41 (4.39)	1968	1892	1917	5.20 (t, 2 H, H_m), 5.41 (d, 2 H, H_o), 5.52 (t, H, H_p)	0.35 (d, 6 H, SiMe), 4.38 (septet, H, SiH)
$\{\eta^6$-1,4-$C_6H_4[Si(Me)_2H]_2\}$-$Cr(CO)_3{}^c$ (**6**)	47.27 (46.98)	5.45 (5.58)	1965	1890	1915	5.25 (5, 4 H, $H_{o,m}$)	0.31 (s, 12 H, SiMe), 4.35 (septet, 2 H, SiH)
$\{\eta^6$-$C_6H_5Si(Me)_2CH{=}CH_2\}$-$Cr(CO)_3$ (**7**)	52.34 (52.55)	4.03 (3.98)	1967	1890	1916	5.17 (t, 2 H, H_m), 5.42 (d, 2 H, H_o), 5.55 (t, H, H_p)	0.38 (s, 6 H, SiMe), 5.68–6.10 (m, 3 H, $SiCHCH_2$)
$\{\eta^6$-$C_6H_5SiMe(NMe_2)_2\}Cr$-$(CO)_3$ (**8**)	48.80 (48.72)	5.80 (5.71)	1965	1888	1913	5.06 (t, 2 H, H_m), 5.35 (d, 2 H, H_o), 5.50 (t, H, H_p)	0.30 (s, 3 H, SiMe), 2.48 (s, 12 H, $Si(NMe_2)$))

[a] ^{1}H NMR run in $CDCl_3$; δ in ppm. [b] ν(CO) (cm^{-1}) values corresponding to the SiO_2 anchored complex in Nujol mull. [c] ν(SiH) (CH_2Cl_2): 2136 cm^{-1} for **5**; 2135 cm^{-1} for **6**.

metal atom have been prepared.[7,8]

In this paper, we would like to report the full details of the synthesis and characterization of a series of chromium tricarbonyl complexes containing reactive organosilane groups on the arene ring. The spectroscopic properties of these new $\{\eta^6$-1,4-$C_6H_4RR'\}Cr(CO)_3$ species are described, as well as their photochemical reactions with tri-*n*-butyl phosphite and their attachment to SiO_2 surfaces. Polymerization reactions for some of the new monomers are described. In addition the electrochemical behavior of all the synthesized complexes is reported and discussed.

Results and Discussion

The novel $\{\eta^6$-(organosilyl)arene$\}$chromium tricarbonyl complexes **1–8** (Chart I), in which a phenyl ring is bound to a silane group, have been prepared by using three methods (eqs 1–3).

$$Cr(CO)_6 + \text{(organosilyl)arene} \xrightarrow[140\ ^\circ C]{n\text{-}Bu_2O/THF\ (9:1,\ v/v)} (\eta^6\text{-(organosilyl)arene})Cr(CO)_3 + 3CO \qquad (1)$$

$$(MeCN)_3Cr(CO)_3 + \text{(organosilyl)arene} \xrightarrow[65\text{–}70\ ^\circ C]{C_6H_{12}} (\eta^6\text{-(organosilyl)arene})Cr(CO)_3 + 3MeCN \qquad (2)$$

$$\begin{tikzcd}
(\eta^6\text{-}C_6H_5Li)Cr(CO)_3 + ClR \arrow[rd, "\text{THF, }-78\ ^\circ C", "-ClLi"'] & \\
& (\eta^6\text{-(organosilyl)arene})Cr(CO)_3 \qquad (3) \\
(\eta^6\text{-}1,4\text{-}C_6H_4Li_2)Cr(CO)_3 + 2ClR \arrow[ru, "\text{THF, }-78\ ^\circ C", "-2ClLi"'] &
\end{tikzcd}$$

Thermal replacement of CO from $Cr(CO)_6$ by the (organosilyl)arenes (eq 1) is the route of choice for the preparation of complexes **1–8** in relatively high yields (65–75%). All reactions have been carried out using an approximately 9:1 mixture (v/v) of n-Bu_2O and THF, as solvent. The reaction times and yields for the various organosilanes studied indicate that reaction 1 is specially facilitated with the more electon-rich arenes as $C_6H_5SiMe(NMe_2)_2$, 1,4-$C_6H_4[Si(Me)_2H]_2$, and 1,4-C_6H_4-$[(CH_2)_2Si(OMe)_3]_2$.

Thermal reaction of (organosilyl)arenes with $(MeCN)_3Cr(CO)_3$ in cyclohexane (eq 2) was also used for the preparation of some $Cr(CO)_3$ complexes. This method is particularly useful for the synthesis of more thermally sensitive species such as $\{\eta^6$-$C_6H_5Si(Me)_2CH{=}CH_2\}Cr$-$(CO)_3$, the reaction being carried out in C_6H_{12} at 60–65 °C. It is also a suitable method to prepare $\{\eta^6$-$C_6H_5Si(Me)_2H\}$- and $\{\eta^6$-1,4-$C_6H_4[Si(Me)_2H]_2\}Cr(CO)_3$ complexes. However using the same reaction conditions it has not been possible to isolate complex $\{\eta^6$-$C_6H_5SiMe(NMe_2)_2\}Cr(CO)_3$ by treatment of $(MeCN)_3Cr(CO)_3$ with bis(dimethylamino)methylphenylsilane.

Another route for the synthesis of complexes **5–8** is based on the treatment of the metalated complexes (η^6-lithiobenzene)$Cr(CO)_3$ and (η^6-1,4-dilithiobenzene)$Cr(CO)_3$ with the corresponding electrophiles. The latter (η^6-1,4-$C_6H_4Li_2)Cr(CO)_3$ was prepared by transmetalation of the $\{\eta^6$-1,4-bis(tri-*n*-butylstannyl)benzene$\}Cr(CO)_3$ compound with 2 molar equiv of *n*-BuLi at −78 °C, according to the valuable method recently described by Wright.[9] Typically, chilled (−78 °C) THF solutions of (η^6-$C_6H_5Li)Cr(CO)_3$ or (η^6-1,4-$C_6H_4Li_2)Cr(CO)_3$ were employed in situ for the treatment with the chlorosilanes $H(Me)_2SiCl$, $(NMe_2)_2MeSiCl$, and $CH_2{=}CH(Me)_2SiCl$.

After these preparations (eqs 1–3) it is necessary to remove some insoluble decomposition materials by filtration through a short column of silanized silica, the resulting bright-yellow solution being concentrated and subjected to column chromatography on silanized silica. Elimination of solvents under vacuum affords the compounds as yellow oils. Trituration of the oil products with *n*-hexane or petroleum ether (40–60 °C) and cooling at ca. −40 °C for several hours (24–48 h) permits isolation of complexes **1** and **5–8** as air- and light-sensitive yellow crystalline solids. Attempts to induce crystallization of **2–4** have not been

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successful, being finally isolated in analytical and pure form as yellow viscous-oil products. The synthesized complexes are very soluble in common organic solvents as CH_2Cl_2, THF, and MeCN, being less soluble in *n*-hexane or pentane. The solutions may be handled under an inert atmosphere. The analytical and selected spectroscopic data of the complexes 1–8 are given in Table I and confirm the proposed formulation (Chart I).

All these complexes exhibit two IR intense bands in the 1970–1880-cm^{-1} region, which on the basis of local C_{3v} symmetry of the $Cr(CO)_3$ group have been assigned to A_1 and E carbonyl stretching vibrations (Table I). However, a splitting (<10 cm^{-1}) or in some cases considerable broadening of the degenerate E ν(CO) band is observed, as it was expected for a small perturbation of C_{3v} symmetry due to the presence of unsymmetrically substituted arenes.[4,10] Table I shows that the IR absorptions of the $Cr(CO)_3$ groups are sensitive to the nature of the organosilane groups on the arene ring. The A_1, E, and $(A_1 + 2E)/3$ frequencies are found to decrease slightly as the electron-donating power of the substituent increases, being the lowest values for complexes **3**, **4**, and **8**.

Photochemical treatment of $\{\eta^6$-(organosilyl)arene$\}Cr(CO)_3$ complexes **1–8** with a nucleophile as tri(*n*-butyl phosphite) in *n*-hexane or cyclohexane solution, at room temperature, gives the monosubstituted dicarbonyl complexes $\{\eta^6$-(organosilyl)arene$\}Cr(CO)_2(P(OBu)_3)$ (**9–16**) (eq 4).

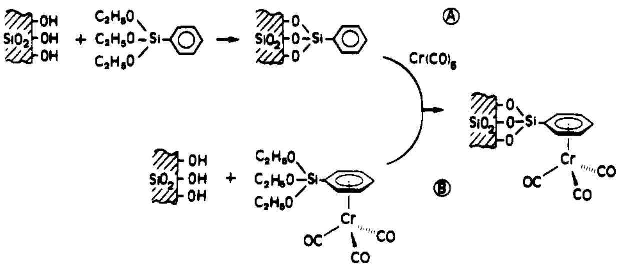
$$\{\eta^6\text{-}1,4\text{-}C_6H_4RR'\}Cr(CO)_3 + P(OBu)_3 \xrightarrow[C_6H_{12}\text{ or }n\text{-hexane}]{h\nu,\ 20\ ^\circ C} \{\eta^6\text{-}1,4\text{-}C_6H_4RR'\}Cr(CO)_2(P(OBu)_3) + CO \quad (4)$$

$R = H, R' = Si(OEt)_3$ (**9**)
$R = H, R' = SiMe(OMe)_2$ (**10**)
$R = H, R' = (CH_2)_2Si(OMe)_3$ (**11**)
$R = R' = (CH_2)_2Si(OMe)_3$ (**12**)
$R = H, R' = Si(Me)_2H$ (**13**)
$R = R' = Si(Me)_2H$ (**14**)
$R = H, R' = Si(Me)_2CH{=}CH_2$ (**15**)
$R = H, R' = SiMe(NMe_2)_2$ (**16**)

The progress of these reactions was monitored by IR spectroscopy. The reaction was completed when the highest ν(CO) band corresponding to the A_1 vibration mode had completely disappeared and new carbonyl bands in the 1840–1850-cm^{-1} region appeared. As in previously reported photosubstitution reactions of $\{\eta^6$-arene$\}Cr(CO)_3$ with phosphites,[4,11,12] the formation of small amounts of the disubstituted products $\{\eta^6\text{-}1,4\text{-}C_6H_4RR'\}Cr(CO)[P(OBu)_3]_2$ was also detected, which were separated from the major dicarbonylic compounds by column chromatography. After this purification, complexes **9–16** were isolated as orange, very air-sensitive oils. The extreme air-sensitivity of these dicarbonylic compounds is consistent with their electrochemical behavior, which reveals relatively low values for the redox potential of the reversible oxidation (see Electrochemical Studies).

Preparation of SiO_2-Supported $\{\eta^6$-(Alkoxysilyl)arene$\}Cr(CO)_3$ Complexes. $\{\eta^6$-Arene$\}Cr(CO)_3$ complexes are known to be efficient catalysts in several processes,[4,13] being unique in forming cis-unsaturated bonds in the hydrogenation of polyunsaturated products.[4,13-16] However, the homogeneous chromium catalysts are impractical for commercial use because they undergo partial decomposition and are difficult to separate from product and recycle. For this reason several studies exist focused on the preparation of heterogenized $\{\eta^6$-arene$\}Cr(CO)_3$ catalysts, by anchoring the homogeneous catalyst to polymeric supports.[14-16]

Scheme I



$\{\eta^6$-(Alkoxysilyl)arene$\}Cr(CO)_3$ complexes **1–4** are suitable organometallic moieties to be attached to inorganic support materials due to the reactivity of the (alkoxysilyl)arene substituents toward surface hydroxyl groups of inorganic oxides as silica, alumina, or zeolites. Two possible synthetic methods for the attachment of the $\{\eta^6$-(alkoxysilyl)arene$\}Cr(CO)_3$ complexes to silica surfaces could be tried, as it was indicated in Scheme I, for the (triethoxysilyl)arene derivative as a representative example.

Method A involves condensation reactions of the (alkoxysilyl)arenes $C_6H_5Si(OEt)_3$, $C_6H_5SiMe(OMe)_2$, and 1,4-C_6H_4RR' ($R = H$, $R' = (CH_2)_2Si(OMe)_3$; $R = R' = (CH_2)_2Si(OMe)_3$) with reactive SiOH groups on the SiO_2 surfaces and subsequent treatment of these arene-functionalized silica compounds with chromium hexacarbonyl. However, we have not followed this procedure because the formation of insoluble decomposition products makes difficult the purification and characterization of the $Cr(CO)_3$-modified silica surfaces.

Method B consists of the previous synthesis of suitable alkoxysilane-functionalized (arene)$Cr(CO)_3$ complexes and subsequent attachment to SiO_2 surfaces. In this way, treatment of the **1–4** compounds with silica gel supports, in toluene at 80 °C, leads to the formation of surface-bound chromium tricarbonyl species. After isolation, the reaction products are yellow materials. Their primary identification was based on their IR spectra, which show two strong ν(CO) bands in the 1980–1880-cm^{-1} region, in close agreement with the corresponding homogeneously dissolved mononuclear complexes **1–4** (Table I). The chromium analyses for the products yield values of ca. 0.3–0.5 mmol of Cr/g of SiO_2.

In preliminary studies these SiO_2-supported $\{\eta^6$-(organosilyl)arene$\}Cr(CO)_3$ derivatives thus obtained, as well as their homogeneous precursors, have been tried as catalysts for the polymerization of phenylacetylene.

We have found that complexes **1–4** catalyze the polymerization of PhC≡CH, in benzene at 80 °C. From these reactions two different compounds can be isolated and separated by column chromatography. One of these compounds is a yellow solid, which on the basis of its melting point and IR and ^1H NMR spectra[13,17] was identified as

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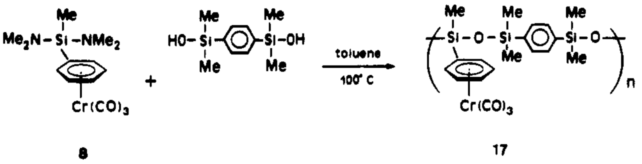
Scheme II



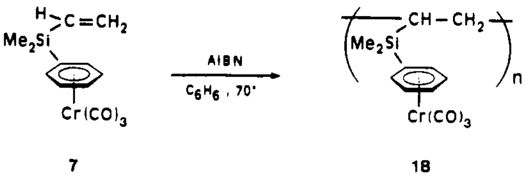
the final poly(phenylacetylene). The other compound is a light-yellow, low-melting-point solid, which was also identified by IR and NMR spectral data as a ladder polymer, composed of fused cyclobutane rings.[18]

However, preliminary results have shown that when, in the polymerization of PhC≡CH, the SiO_2-supported chromium tricarbonyl complexes were used as the catalyst, only the ladder intermediate was formed, the formation of the final poly(phenylacetylene) not being detected. It seems that, in the presence of these SiO_2-supported Cr(CO)$_3$ catalysts, the conversion of the ladder intermediate into the lineal polyconjugated poly(phenylacetylene) is hindered.

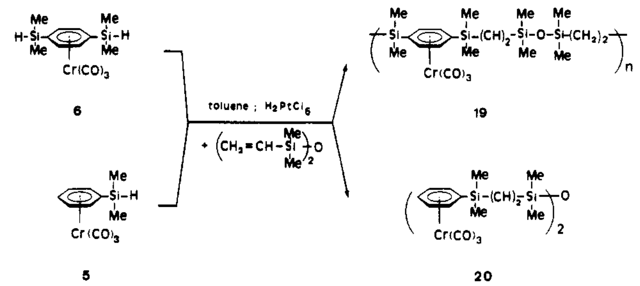
Polynuclear and Dinuclear Cr(CO)$_3$ Complexes. A number of macromolecular (η^6-arene)chromium tricarbonyl complexes are known.[2,14–16,20,21] Generally they have been obtained by reaction, at high temperatures, of Cr(CO)$_6$ with polymers containing arene rings as polystyrene and linear or ladder poly(phenyl- or poly(methylphenylsiloxanes). However, for the siloxane–Cr(CO)$_3$ polymers this method presented several problems because the elevated temperatures and long reaction periods caused noticeable decomposition. Furthermore, during the complexation reaction of the Cr(CO)$_3$ group to the phenyl rings, a competitive siloxane-chain scission reaction takes place, resulting that the most highly complexed polymers were generated with a sacrifice in the molecular weights.[14,20] We therefore undertook a study of the synthesis of new siloxane polymers with chromium tricarbonyl fragments, by using a synthetic method that starts from Cr(CO)$_3$ monomers. Some of the novel mononuclear $\{\eta^6$-(organosilyl)arene$\}$Cr(CO)$_3$ complexes (namely **6**–**8**) are suitable precursors in the preparation of new polymer–Cr(CO)$_3$ compounds because of the reactivity of the Si–NMe_2, Si–CH=CH_2, and Si–H groups of the arene ring.

Polycondensation of **8** with 1,4-bis(hydroxydimethylsilyl)benzene was carried out in toluene solvent (Scheme II). The process was started at room temperature with subsequent slow heating to 100–110 °C; the mixture was then warmed to 50–60 °C in vacuum for 1 h. After purification by repeated precipitation from a small volume of toluene by addition to a large volume of rapidly stirred, dried, and degassed methanol, the polymer [–SiMe$\{\eta^6$-$C_6H_5\}$Cr(CO)$_3$OSiMe$_2$(1,4-C_6H_4)SiMe$_2$O–]$_n$ (**17**) was isolated as a yellow rubberlike product. The ^{1}H NMR spectrum (in $CDCl_3$ solution) of this compound confirms the total absence of signals corresponding to the methyl resonances of the Si(NMe_2) group, which are observed at 2.48 ppm in the ^{1}H NMR spectrum of the monomer **8**. The absence in the polymer of the Si(NMe_2) groups and the presence of the Si–O–Si bonds are also supported by the IR spectrum.

Scheme III



Scheme IV



$\{\eta^6$-Phenyldimethylvinylsilane$\}$chromium tricarbonyl (**7**), in benzene solution, at 80 °C, undergoes homopolymerization in the presence of azobis(isobutyronitrile) (AIBN) as initiator (Scheme III). Polymer **18** was purified as we described above, being isolated as a yellow fibrous solid. Its ^{1}H NMR spectrum ($CDCl_3$ solution) shows the absence of the vinylic proton resonances, which are observed at 6.10–5.68 ppm in the spectrum of the monomer **7**. The IR spectrum of [–CH_2CH$\{\eta^6$-$C_6H_5SiMe_2\}$Cr(CO)$_3$–]$_n$ (**18**) shows no bands assignable to the C=C double bonds of the monomer.

On the other hand, addition of complex $\{\eta^6$-1,4-C_6H_4-[SiMe$_2$H]$_2\}$Cr(CO)$_3$ (**6**) to 1,3-divinyltetramethyldisiloxane was also studied. The hydrosilylation reaction was performed in toluene solvent, at 85 °C, and using hexachloroplatinic acid as catalyst (Scheme IV), the compound [–SiMe$_2\{\eta^6$-1,4-$C_6H_4\}$Cr(CO)$_3$SiMe$_2$(CH$_2$)$_2$SiMe$_2$OSi(CH$_2$)$_2$–]$_n$ (**19**) being isolated. We have also prepared the dinuclear model complex $\{\eta^6$-C_6H_5SiMe$_2$(CH$_2$)$_2$SiMe$_2$–$\}_2$O-[Cr(CO)$_3$]$_2$ (**20**) by reaction of 2 mol equiv of **5** with (CH_2=CH–SiMe$_2$)$_2$O. The progress of both hydrosilylation processes was monitored by IR spectroscopy, being finished when the strong ν(Si–H) band had completely disappeared. ^{1}H NMR spectra of **19** and **20** show no bands assignable to the SiH protons of the Si(Me)$_2$H groups, observed as a septet at 4.38 ppm for **5** and 4.35 ppm for **6**.

The novel organosiloxane polynuclear Cr(CO)$_3$ compounds **17**–**19** are much less soluble in organic solvents than the monomers precursors but soluble enough in CH_2Cl_2 and $CDCl_3$ for electrochemical and spectroscopic studies.

Electrochemical Studies

Electrochemistry of Mononuclear Complexes. The oxidative electrochemistry of the synthesized compounds was studied in dichloromethane, propylene carbonate (PC), and acetonitrile with 0.10 M Bu_4NPF_6 as supporting electrolyte. Electrochemical parameters of the complexes are summarized in Table II. On the cyclic voltammetry time scale, the chemical reversibility of the oxidation is very dependent on the solvent.

In dichloromethane, the cyclic voltammograms of compounds **1**–**7** show an anodic peak, A, and the corresponding

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(17) (a) Woon, P. S.; Farona, M. F. *J. Polym. Sci. Polym. Chem. Educ.* **1974**, *12*, 1749. (b) Farona, M. F.; Lofgren, P. A.; Woon, P. S. *J. Chem. Soc., Chem. Commun.* **1974**, 246.

(18) This ladder compound is an intermediate in the polymerization of phenylacetylene catalyzed by arene-group 6 tricarbonyls. It undergoes catalytic isomerization to the final polyconjugated polymer; see refs 13 and 17.

(19) Related studies on reactions of diphenylacetylene with carbon monoxide catalyzed by polystyrene-supported molybdenum have been reported; see: (a) Vatanatham, S.; Farona, M. F. *J. Catal.* **1980**, *61*, 540. (b) Vatanatham, S.; Farona, M. F. *J. Mol. Catal.* **1980**, 403.

(20) Pittman, C. U., Jr.; Patterson, W. J.; McManus, S. P. *J. Polym. Sci. Polym. Chem. Educ.* **1975**, *13*, 39.

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Table II. Cyclic Voltammetric Data (vs SCE) for the Oxidation of the $\{\eta^6\text{-(Organosilyl)arene}\}Cr(CO)_3$ Complexes[a]

complex	solvent	E_p(A), V	ΔE_p, mV	E_p(B), V	$(E_p(D) + E_p(D'))/2$, V
$\{\eta^6\text{-}C_6H_5Si(OEt)_3\}Cr(CO)_3$ (1)	CH_2Cl_2	1.06	120	1.73	0.33
	PC	0.96		1.72	0.29
	CH_3CN	0.97			
$\{\eta^6\text{-}C_6H_5SiMe(OMe)_2\}Cr(CO)_3$ (2)	CH_2Cl_2	1.08	150	1.78	0.34
	PC	0.95		1.72	0.30
	CH_3CN	0.96			
$\{\eta^6\text{-}C_6H_5(CH_2)_2Si(OMe)_3\}Cr(CO)_3$ (3)	CH_2Cl_2	0.96	100	1.68	0.31
	PC	0.86		1.65	0.28
	CH_3CN	0.90			
$\{\eta^6\text{-}1,4\text{-}C_6H_4[(CH_2)_2Si(OMe)_3]_2\}Cr(CO)_3$ (4)	CH_2Cl_2	0.92	75	1.65	0.30
	PC	0.85	70	1.64	0.28
	CH_3CN	0.90			
$\{\eta^6\text{-}C_6H_5Si(Me)_2H\}Cr(CO)_3$ (5)	CH_2Cl_2	1.04	120	1.70	0.33
	PC	0.94		1.68	0.30
	CH_3CN	0.96			
$\{\eta^6\text{-}1,4\text{-}C_6H_4[Si(Me)_2H]_2\}Cr(CO)_3$ (6)	CH_2Cl_2	1.00	77	1.72	0.35
	PC	0.89	70	1.69	0.32
	CH_3CN	0.95			
$\{\eta^6\text{-}C_6H_5Si(Me)_2CH{=}CH_2\}Cr(CO)_3$ (7)	CH_2Cl_2	0.98	155	1.68	0.36
	PC	0.88		1.65	0.32
	CH_3CN	0.90			
$\{\eta^6\text{-}C_6H_5SiMe(NMe_2)_2\}Cr(CO)_3$ (8)	CH_2Cl_2	0.97	*b*	1.20, B_1; 1.42, B_2[c]	0.30
	PC	0.88			0.32
	CH_3CN	0.90			
$[-SiMe\{\eta^6\text{-}C_6H_5\}Cr(CO)_3OSiMe_2(1,4\text{-}C_6H_4)SiMe_2O-]_n$ (17)	CH_2Cl_2	0.99	84	1.53	
	PC	*d*			
$[-CH_2CH\{\eta^6\text{-}C_6H_5SiMe_2\}Cr(CO)_3-]_n$ (18)	CH_2Cl_2	0.94	65	1.50	
	PC	0.87		1.48	
$[-SiMe_2\{\eta^6\text{-}1,4\text{-}C_6H_4\}Cr(CO)_3SiMe_2(CH_2)_2SiMe_2OSi(CH_2)_2-]_n$ (19)	CH_2Cl_2	0.79	80		
	PC	*d*			
$\{\eta^6\text{-}C_6H_5SiMe_2(CH_2)_2SiMe_2\}_2O[Cr(CO)_3]_2$ (20)	CH_2Cl_2	1.00	70	1.60	
	PC	0.88		1.68	

[a] Unless otherwise noted, scan rate v = 200 mV/s at room temperature. [b] At −30 °C, E_p(A) = 1.06 V, ΔE_p = 210 mV. [c] See text. [d] Sparingly soluble compound.

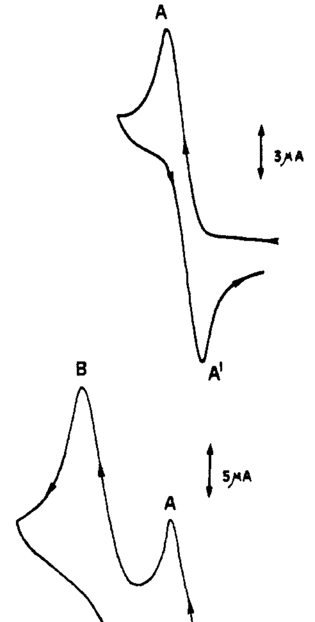

Figure 1. Cyclic voltammograms of 1×10^{-3} M $\{\eta^6\text{-}1,4\text{-}C_6H_4[Si(Me)_2H]_2\}Cr(CO)_3$ (6) in 0.10 M Bu_4NPF_6/CH_2Cl_2, at 200 mV/s at a glassy-carbon disk electrode.

cathodic peak A′ (Figure 1; Table II). In all cases the ratio of cathodic to anodic currents i_{pc}/i_{pa} was very close to unity, and the peak separation, ΔE_p, was dependent on concentration. These electrochemical processes, and those described later, are diffusion controlled with the anodic current function ($i_{pa}/v^{1/2}$) independent of the scan rate (v) over the scan range studied. Potentiostatic coulometry and comparisons of limiting currents, obtained from rotating-disk-electrode (RDE) voltammograms for 1–7 with those of ferrocene, indicate a one-electron exchange in these oxidation steps. These results indicate that for compounds 1–7 chemically reversible processes take place, and stable monocations, in the CV time scale, are formed. The existence of these monocationic species has been proved by controlled-potential electrolysis of $\{\eta^6\text{-}1,4\text{-}C_6H_4RR'\}Cr(CO)_3$ complexes in the EPR cavity. The paramagnetic species formed in the oxidation step (at potentials 100 mV more positive than E_p(A)) show, in frozen solution (at −120 °C), a rhombic spectrum with 3-fold anisotropy of the g factor, which correspond to 17-electron oxidized species $[\{\eta^6\text{-}1,4\text{-}C_6H_4RR'\}Cr(CO)_3]^+$ ($g_1 = 2.100$, $g_2 = 2.024$, $g_3 = 1.990$ for complex 6).

When the sweep range is extended, the cyclic voltammograms of the complexes display another anodic peak, B. These oxidations are irreversible at scan rates as high as 5 V/s, i_p(B) being very similar to i_p(A); these peaks can be ascribed to the oxidation of $[\{\eta^6\text{-}1,4\text{-}C_6H_4RR'\}Cr(CO)_3]^+$ to $[\{\eta^6\text{-}1,4\text{-}C_6H_4RR'\}Cr(CO)_3]^{2+}$.

In CH_2Cl_2, complex $\{\eta^6\text{-}C_6H_5SiMe(NMe_2)_2\}Cr(CO)_3$ (8) exhibits a different electrochemical behavior. At low scan rates and at room temperature the first oxidation process, corresponding to one-electron transfer, is irreversible as shown by the complete absence of a cathodic peak. However at low temperatures (−35 °C) and high scan rates (v > 2 V/s) 8 undergoes a partially chemically reversible oxidation, the i_{pc}/i_{pa} ratio being >0.66. The average values of the first-order constant, k_f,[22] for the decomposition of

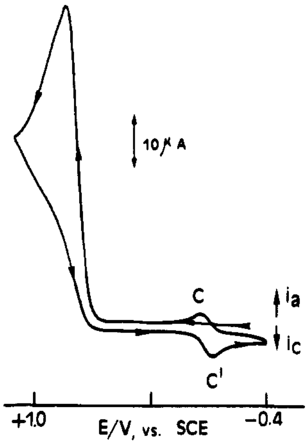

Figure 2. Cyclic voltammogram of 1 × 10^{-3} M $\{\eta^6\text{-}C_6H_5Si(OEt)_3\}Cr(CO)_3$ (1) in 0.10 M Bu_4NPF_6/MeCN at 200 mV/s at a glassy-carbon disk electrode.

8^+ are 2.55 ± 0.5 s^{-1} at 0 °C and 0.44 ± 0.5 s^{-1} at −35 °C. When the anodic potential limit is increased, the cyclic voltammogram shows other two anodic irreversible peaks, B_1 and B_2 (Table II). It is quite significant that in this case the peak B_1 is 0.23 mV more positive than E_p(A), while in the case of other complexes it is ca. 0.65 mV more anodic. The peak B_1 corresponds closely to the oxidation of the free arene $C_6H_5SiMe(NMe_2)_2$. The instability of the cation $[\{\eta^6\text{-}C_6H_5SiMe(NMe_2)_2\}Cr(CO)_3]^+$ could be related to the oxidation of the ligand. A similar behavior has been observed for other NMe_2-substituted arene ligands.[23,24]

In propylene carbonate the oxidation of complexes 1–7 is partially chemically reversible. At room temperature and slow rates the cathodic peak A′ is not detected. However this peak appears when the sweep rates are increased and the temperature is decreased. The enhanced stability observed for these species in dichloromethane over propylene carbonate may arise from ion-pairing of the cation with PF_6^- anion, which should be stronger in less polar CH_2Cl_2.[25,26] The stability of the cations is greatly affected by the substitution of the 1,4-positions on the phenyl ring, which produces a dramatic increase in the lifetime of the cations $[\{\eta^6\text{-}1,4\text{-}C_6H_4[(CH_2)_2Si(OMe)_3]_2\}Cr(CO)_3]^+$ and $[\{\eta^6\text{-}1,4\text{-}C_6H_4[Si(Me)_2H]_2\}Cr(CO)_3]^+$, as shown by a ratio of i_c/i_a very close to unity, even at room temperature.

Using MeCN as solvent, the oxidation peak is irreversible, as shown by the complete absence of cathodic peak, even at high scan rates. On the reverse sweep a new reversible wave, C/C′, absent on the initial scan in this region can be detected, with $E_{1/2}$ = −0.015 V vs SCE (Figure 2). This observed redox potential corresponds closely to the observed for $(MeCN)_3Cr(CO)_3{}^{0/+}$ chemically obtained.[27] These results are consistent with an electrochemical EC mechanism, the $[(MeCN)_3Cr(CO)_3]^+$ intermediate being detected on the reverse sweep:

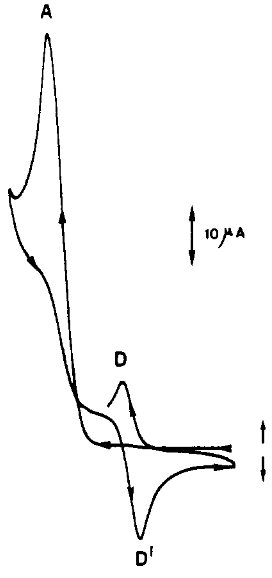

Figure 3. Cyclic voltammogram of 1 × 10^{-3} M $\{\eta^6\text{-}1,4\text{-}C_6H_4[Si(Me)_2H]_2\}Cr(CO)_3$ (6) and 4 × 10^{-3} M $P(OBu)_3$ in 0.10 M Bu_4NPF_6/CH_2Cl_2, at 200 mV/s at a glassy-carbon disk electrode.

$$[\{\eta^6\text{-}1,4\text{-}C_6H_4RR'\}Cr(CO)_3] \underset{}{\overset{-e^-}{\rightleftharpoons}} [\{\eta^6\text{-}1,4\text{-}C_6H_4RR'\}Cr(CO)_3]^+ \quad (5)$$

$$[\{\eta^6\text{-}1,4\text{-}C_6H_4RR'\}Cr(CO)_3]^+ + 3MeCN \xrightarrow{k_f} [(MeCN)_3Cr(CO)_3]^+ + C_6H_4RR' \quad (6)$$

The variation of the anodic potential peak, E_{pa}, with scan rate (v) corresponds to a totally irreversible electron transfer.[28]

In general, the cations $[\{\eta^6\text{-}1,4\text{-}C_6H_4RR'\}Cr(CO)_3]^+$ are more stable when the solvent is nonnucleophilic or when the substituents on the arene ring are donating groups. This evidence suggests that the attack by the solvent is the initial step in the decomposition of $[\{\eta^6\text{-}1,4\text{-}C_6H_4RR'\}Cr(CO)_3]^+$. In agreement with this, the presence of sterically congested arenes in the complexes leads to an increase in the stability of the cations. The steric bulk around the phenyl ring, caused by the substitution in the 1,4-positions and/or bulkier substituents, retards the attack of nucleophiles.[29,30]

Induced Ligand Substitution. When complexes 1–8 are oxidized, in the presence of $P(OBu)_3$, in nonnucleophilic solvents (CH_2Cl_2, PC), we found drastic changes in the recorded cyclovoltammograms. As shown in Figure 3, the reversibility of the A/A′ systems disappears and a little shift of E_p(A) toward positive potentials is detected. Moreover a new chemically reversible couple D/D′ appears at a less positive potential (Table II), which can be assigned to the system $[\{\eta^6\text{-}1,4\text{-}C_6H_4RR'\}Cr(CO)_2P(OBu)_3]/[\{\eta^6\text{-}1,4\text{-}C_6H_4RR'\}Cr(CO)_2P(OBu)_3]^+$, as is shown from the cyclovoltammograms of complexes $\{\eta^6\text{-}1,4\text{-}C_6H_4RR'\}Cr(CO)_2P(OBu)_3$ (9–16) photochemically synthesized.

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[25] Ion pairing by PF_6^- has been postulated as being responsible for the enhanced stability of a number of organometallic cations, including that derived from $\{\eta^6\text{-benzene}\}Cr(CO)_3$: Stone, N.; Sweigart, D.; Bond, A. M. *Organometallics* **1986**, *5*, 2553.

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The EPR spectra of the products of controlled-potential electrolysis of the tricarbonyl complexes in CH_2Cl_2 (carried out at $E > E_{pa}$) in the cavity of an EPR spectrometer in the presence of added $P(OBu)_3$ were recorded. At −120 °C, the formed species show EPR signals, with three g-factor values and ^{31}P hyperfine coupling ($g_1 = 2.095$, $g_2 = 2.019$, $g_3 = 1.985$; $A_1 = 25.9$ G, $A_2 = 30.2$ G, $A_3 = 29.2$ G for complex **6**).

The formation of the monosubstituted phosphite cations $[\{\eta^6\text{-}1,4\text{-}C_6H_4RR'\}Cr(CO)_2P(OBu)_3]^+$ was also suggested by the results obtained from in situ FT-IR spectroelectrochemical studies. Figure 4 shows the infrared spectral changes that accompany the controlled-potential electrolysis of $\{\eta^6\text{-}C_6H_5Si(OEt)_3\}Cr(CO)_3$ (**1**), in the presence of an excess of $P(OBu)_3$, in CH_2Cl_2. The initial ν(CO) carbonyl peaks at 1965 and 1890 cm^{-1} due to the parent **1** decrease in intensity upon oxidation, while new carbonyl bands grow at 1915 and 2020 cm^{-1}. These frequency values are consistent with those expected for cationic species like $[(\eta^6\text{-arene})Cr(CO)_2L]^+$, where L is a phosphorous ligand.[26,31-33] If electrolysis times last longer than a few minutes, other weak IR bands, probably due to decomposition products, appear in this region.

The results obtained can be explained by the following mechanism:

$$\underset{\text{I}}{[\{\eta^6\text{-}1,4\text{-}C_6H_4RR'\}Cr(CO)_3]} \underset{E^\circ_1}{\overset{-e^-}{\rightleftharpoons}} \underset{\text{I}^+}{[\{\eta^6\text{-}1,4\text{-}C_6H_4RR'\}Cr(CO)_3]^+} \quad (7)$$

$$[\{\eta^6\text{-}1,4\text{-}C_6H_4RR'\}Cr(CO)_3]^+ \xrightarrow{k,\,L} \underset{\text{II}^+}{[\{\eta^6\text{-}1,4\text{-}C_6H_4RR'\}Cr(CO)_2L]^+} \quad (8)$$

$$[\{\eta^6\text{-}1,4\text{-}C_6H_4RR'\}Cr(CO)_2L]^+ \underset{E^\circ_2}{\overset{+e^-}{\rightleftharpoons}} \underset{\text{II}}{[\{\eta^6\text{-}1,4\text{-}C_6H_4RR'\}Cr(CO)_2L]} \quad (9)$$

$$L = P(OBu)_3$$

Crossing between cathodic and anodic CV traces is observed in Figure 3. Similar phenomena have been observed for several systems and electrochemically induced processes.[34,35] They appear as being characteristic of electrochemical inducement of chemical reactions when the product redox couple has a standard potential negative compared to that of the reactant redox couple (oxidation–reduction induction case).

During the anodic scan, II$^+$ is produced in appreciable amounts only when the potential reaches the oxidation region of I; II$^+$ is electrochemically stable in this potential zone, $E^\circ_2 < E_1$. In the reverse scan II$^+$ remains stable as long as the potential does not exceed E°_2. Therefore, II$^+$ diffuses toward the solution and reacts with I, which diffuses toward the electrode according to the reaction

$$\text{II}^+ + \text{I} \rightleftharpoons \text{I}^+ + \text{II} \quad (10)$$

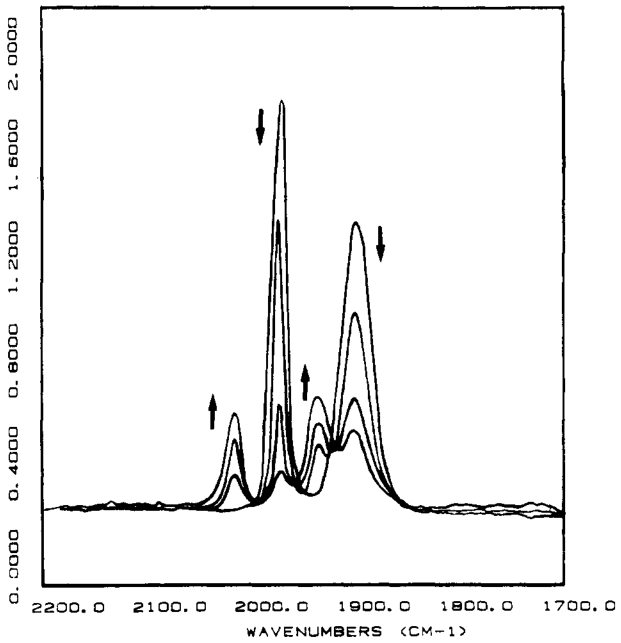

Figure 4. Infrared spectral changes observed upon oxidation of 5×10^{-3} M **1** and 2×10^{-2} M $P(OBu)_3$ in 0.20 M Bu_4NPF_6/CH_2Cl_2 at +1.4 V vs the Ag pseudoreference, in the spectroelectrochemical cell, at room temperature (total elapsed time 10 min).

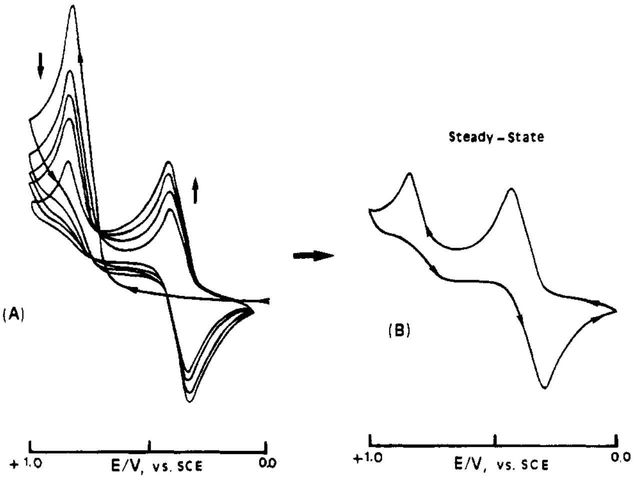

Figure 5. (A) Repetitive (five-cycle) cyclic voltammogram of 1×10^{-3} M **6** and 4×10^{-3} M $P(OBu)_3$ in 0.10 M Bu_4NPF_6/CH_2Cl_2, at 200 mV/s at a glassy-carbon disk electrode. (B) Steady-state CV after 25 cycles.

This is an endergonic reaction, but its coupling to reaction 8 drives it toward the formation of II$^+$ according to the overall reaction

$$\text{II}^+ + \text{I} \longrightarrow \text{II} + \text{II}^+ \quad (11)$$

Then II can be oxidized at the electrode, giving rise to an anodic current. It follows that the I/I$^+$ couple initially present in the diffusion layer is rapidly converted into the II/II$^+$ couple. The magnitude of the curve crossing is more pronounced at slower scan rates.

When the CV was repeatedly cycled between +0.0 and +1.0 V vs SCE, it is attained the steady-state cyclic voltammogram and two isopotential[35] points were detected (Figure 5), which indicate that one electroactive species is quantitatively converted to another.

With propylene carbonate as solvent the reversible couple corresponding to II/II$^+$ is also observed when $P(OBu)_3$ is added, but the curve crossing is detected only

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(33) Recent IR spectroelectrochemical studies on the oxidation of the related complex $\{\eta^6\text{-mesitylene}\}W(CO)_3$ in presence of $P(OBu)_3$ have been reported: Zhang, Y.; Gosser, D. K.; Rieger, P. H.; Sweigart, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 4062.

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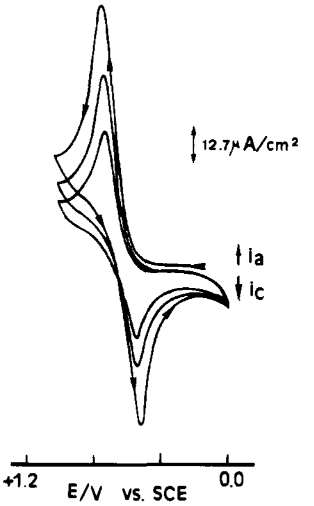

Figure 6. Cyclic voltammogram for a platinum electrode silanized with complex $\{\eta^6\text{-}C_6H_5(CH_2)_2Si(OMe)_3\}Cr(CO)_3$ (**3**) and cycled at various scan rates in 0.10 M Bu_4NPF_6/CH_2Cl_2.

at lower scan rates (v < 50 mV/s). This behavior is in agreement with the higher viscosity of PC that makes difficult the diffusion of II^+ and I.

The trace-crossing phenomenon is related to an autocatalytic process originated from reaction 10 provided this is not too slow as compared with diffusion.

Chemical Modification of Platinum Electrodes. We have studied the electrochemistry of modified Pt electrodes by attachment of complexes **1**–**4**. Figure 6 shows cyclic voltammograms of $\{\eta^6\text{-}C_6H_5(CH_2)_2Si(OMe)_3\}Cr(CO)_3$ (**3**) surface attached via silanization, in CH_2Cl_2, 0.1 M Bu_4NPF_6. The amount of electroactive material is given by the area under the voltammograms; surface coverage was determined to be 4.22×10^{-9} mol/cm².[36] A wave for the surface-bound complex is observed at a potential of $E_{1/2} = 0.86$ V. This value is very near that 0.91 V found for the nonattached complex in CH_2Cl_2 solution. The surface wave exhibits the symmetry, small peak potential separation ($\Delta E_p \approx 50$ mV at $v < 20$ mV s^{-1}), and peak current-potential scan-rate proportionality corresponding to a surface-immobilized species charge-transfer state.[37] The silanized electrodes gave significantly larger peak-to-peak separations and negative deviations from current linearity at higher sweep rates, indicating increased resistance to counterion movements.[38]

The thickness of the silanized films increase with the length of time the electrode is exposed to the silylated complex and with the increasing temperature. For these thick films the electrode kinetics are slow, as it is shown by the greatly increased peak separations (ΔE_p) and widths.

A moderately rapid loss of electroactive material was observed on repeated scans, the rate increasing with the scan rate. A possible hypothesis to account for the dependance on sweep rate is that the film is disrupted by the movement of counterions accompanying the flow of current.[39] Therefore, the instability of electrode reaction products appears to be associated not only with the degradation of the immobilizing Pt–O–Si bonds.

Dinuclear and Polynuclear Complexes. The dinuclear complex **20** shows a reversible oxidation ($E_p(A) = +1.00$ V, vs SCE at 0.2 V/s) in CH_2Cl_2, at room temperature. Another irreversible peak is observed, which is 600 mV more anodic than the first oxidation wave. Potentiostatic coulometry and comparison of the limiting currents from rotating-disk-electrode (RDE) voltammograms with the mononuclear complex **5** indicate that a two-electron transfer is associated with the first peak. Persistence and stability of the cation are greatly affected by the temperature and solvent employed. The compound shows only a small cathodic peak when cyclics are performed at 200 mV s^{-1} and room temperature in PC. The reversibility is increased when higher sweep rates are used. When the temperature is lowered, the lifetime of the cation increases.

The observed electrochemical behavior of the polymers **17**–**19** in CH_2Cl_2 and PC solutions is similar to that displayed by the respective precursor mononuclear complexes, a slight shift being detected of the first oxidation peak to more anodic potentials as well as an increase in the stability of the resulting cationic species.

The results obtained in the electrochemical study of complexes **17**–**20** are consistent with the noninteracting character of the equivalent electroactive groups in the compounds.[23]

In the case of the polymer **17** we have found a very different behavior compared to that of the corresponding parent complex **8**. The first oxidation process of the polymer is completely chemically reversible; this contrasts with the instability shown by the cation 8^+. It is quite significant that in the polymer the (dimethylamino)silane substituents, $C_6H_5Si(NMe_2)_2Me$, are absent as a result of the condensation reaction. Thus, it seems reasonable to associate the instability of the cation 8^+ with the presence of the $C_6H_5Si(NMe_2)_2Me$ arene in the molecule, as was indicated above.

Experimental Section

General Data. All reactions and subsequent manipulations of compounds and solvents were carried out under a nitrogen atmosphere by using conventional Schlenk techniques, the light-sensitive derivatives being manipulated in the dark. Solvents were degassed and purified by distillation under nitrogen from standard drying agents.[40–42] In particular, di-*n*-butyl ether, Bu_2O, was distilled from CaH_2.

Syntheses of $(MeCN)_3Cr(CO)_3$,[43] $(\eta^6\text{-}C_6H_5Li)Cr(CO)_3$,[44] $(\eta^6\text{-}1,4\text{-}C_6H_4Li_2)Cr(CO)_3$,[9] and 1,4-bis(tributylstannyl)benzene[45] were carried out according to published procedures. Tributyltin chloride and *n*-BuLi (2.5 M in hexane) were purchased from Aldrich Chemical Co. and used as received. Tri-*n*-butyl phosphite (Fluka) was distilled under N_2 at reduced pressure prior to use. The following phenylsilanes were purchased from Petrarch Systems Inc. and used as received: phenyltriethoxysilane, phenylmethyldimethoxysilane, phenyldimethylvinylsilane, phenyldimethylsilane, bis(dimethylamino)methylphenylsilane, phenethyltrimethoxysilane, 1,4-bis((trimethoxysilyl)ethyl)benzene, and 1,4-bis(dimethylsilyl)benzene. 1,4-Bis(hydroxydimethylsilyl)benzene (Petrarch) was purified by recrystallization from CCl_4. The chlorosilanes (Petrarch) bis(dimethylamino)methylchlorosilane, and vinyldimethylchlorosilane were distilled in vacuum,

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and dimethylchlorosilane was used as received. Chloroplatinic acid solution was used as a catalyst for hydrosilylation, being prepared from 1 g of chloroplatinic acid (Strem) in 9 mL of 1,2-dimethoxyethane and 1 mL of absolute 2-propanol. Azobis(isobutyronitrile) (AIBN) (Fluka) was recrystallized from methanol.

Column chromatographic purifications of the complexes were performed with silanized silica gel 60 (70–230 mesh) from Merck. The support material used for the preparation of the attached $Cr(CO)_3$ complexes described below is made of silica gel 100 (Merck, 0.063–0.200-mm 70–230 mesh), which was refluxed in dry methanol under dry nitrogen and dried in vacuum as it was previously described.[46]

Infrared spectra were recorded on a Nicolet 5 DX FT-IR spectrometer. The solution spectra were examined in a 0.1-mm KBr solution cell. Nuclear magnetic resonance spectra were recorded on a Bruker WH-200-5Y (200 MHz, FT mode) spectrometer. The ^1H chemical shifts are reported in parts per million (δ) with reference to internal Me_4Si. Elemental analyses were performed by the Microanalytical Laboratory, Department of Chemistry, Universidad Autônoma de Madrid, Madrid, Spain. Number-average molecular weights ($\bar{M}_n$) were obtained with a Knauer vapor-pressure osmometer. Photochemical reactions were carried out under N_2, in an Ace & Glass Inc. photochemical reactor using a cooled medium-pressure Hanovia 450-W mercury vapor lamp.

Electrochemical Procedures. All electrochemical experiments were carried out under a blanket of dry nitrogen that was saturated with the solvent in use. Dichloromethane and acetonitrile were freshly distilled under nitrogen from calcium hydride. Propylene carbonate (PC) was purified by distillation in vacuum and stored refrigerated. Tetra-*n*-butylammonium hexafluorophosphate (Bu_4NPF_6) was purchased from BAS or Strem and purified by recrystallization from ethanol and dried in vacuum at 60 °C. All electrochemical experiments were performed at ambient temperature unless otherwise noted.

Cyclic voltammetry was done with a PAR EG&G 362 potentiostat in a three-electrode configuration; the voltammetric data were recorded with a Nicolet 310 digital oscilloscope or a Linseis LY-17100 X-Y recorder. The working electrode was a platinum or glassy-carbon disk (diameter 3.0 mm) and the counter electrode was a platinum wire. The reference electrode was a saturated calomel electrode (SCE), which was separated from the test solution by a salt bridge containing (Bu_4NPF_6) (0.10 M) in the corresponding solvent in use. The working compartment of the electrochemical cell was separated from the reference compartment by a modified Luggin capillary. All potentials reported in this paper are referenced to the aqueous SCE. $E°$ for the ferrocinium/ferrocene couple in CH_2Cl_2/Bu_4NPF_6 was $E° = +0.400$ V; in acetonitrile/Bu_4NPF_6 $E° = +0.395$ V and in PC/Bu_4NPF_6 $E° = +0.385$ V. No *iR* compensation was used.

Bulk electrolysis was done with a PAR EG&G 362 potentiostat and a 379 digital coulometer. A PAR EG&G 377A coulometry cell system fitted with platinum-gauze working electrode was used. The counter electrode was a platinum mesh, which was separated from the working electrode by a salt bridge containing the supporting electrolyte.

Spectroelectrochemical Experiments. IR spectroelectrochemistry was performed with thin-layer spectroelectrochemical cell constructed by following approximately a previously described model.[47] The cell chamber is formed directly from a commercial microcavity IR cell (path length of 0.2 mm) purchased from Aldrich Chemical Co. The FT-IR cell utilizes a three-electrode configuration. The working electrode is a 52-mesh platinum gauze woven from a 0.1 mm diameter wire (Johnson Matthey). The transparency of this platinum electrode is about 50% as measured by the intensity of the IR interferogram. The working electrode connection is made through a 0.25-mm platinum wire and is insulated from the solution by a Teflon film. The counter electrode is a platinum wire, and the reference is a silver wire. Transfer of deoxygenated solutions into the IR cell is done with a 100-μL syringe using Schlenk techniques. The spectra were recorded on a FT-IR Nicolet 5 DX spectrometer with a routine consisting of 24 scans and a resolution of 2 cm^{-1}. The potential was applied with a PAR EG&G 362 potentiostat.

X-Band EPR spectra were recorded on a Varian E-12 spectrometer equipped with a HP-5342A frequency meter and a Bruker NMR gaussmeter. The EPR studies were performed by using a spectroelectrochemical cell as we described previously.[8]

Silanization. Mirror-polished (1-μm diamond paste) Pt-disk electrodes (area 0.785 cm^2) are prepared for silane chemical modification, using an initial 5-min anodization, in 0.5 M H_2SO_4 at 1.9 V vs SCE, followed by cycling between 1.23 and −0.25 V (100 mV/s) until the current decays to small value (<1 $\mu A/cm^2$ at 1.1 V). The anodized electrode is removed from the cell, washed thoroughly with distilled water and methanol, and vacuum oven dried (20–45 min, 50 °C).

The electrodes were placed in Schlenk tubes maintained under N_2 and containing the respective (alkoxysilyl)arene complexes 1–4 in *n*-heptane solution. The reaction temperature was maintained between 25 and 70 °C and the reaction time varied from 2 to 6 h. The electrodes were then removed from solution, rinsed several times with dry dichloromethane, dried, and stored under vacuum.

Preparation of the Complexes $\{\eta^6\text{-1,4-}C_6H_4RR'\}Cr(CO)_3$. Three different methods were used for the synthesis of the new $\{\eta^6$-(organosilyl)arene$\}$chromium tricarbonyl complexes reported in this study. For each one of these methods, the described reactions were performed in a similar manner. The procedures for $\{\eta^6\text{-}C_6H_5Si(OEt)_3\}Cr(CO)_3$ (1), $\{\eta^6\text{-}C_6H_5Si(Me)_2CH{=}CH_2\}Cr(CO)_3$ (7), $\{\eta^6\text{-}C_6H_5Si(NMe_2)_2Me\}Cr(CO)_3$ (8) and $\{\eta^6\text{-1,4-}C_6H_4[Si(Me)_2H]_2\}Cr(CO)_3$ (6) are described in detail as representative examples. The analytical and spectroscopic data for all the complexes are given in Table I.

Method A:

$$Cr(CO)_6 + (1,4\text{-}C_6H_4RR') \rightarrow \{\eta^6\text{-1,4-}C_6H_4RR'\}Cr(CO)_3 + 3CO$$

$\{\eta^6\text{-}C_6H_5Si(OEt)_3\}Cr(CO)_3$ (1). The reaction was carried out in a 250-mL, three-necked round-bottomed flask equipped with a gas inlet and a straight-tube condenser topped with gas inlet and bubbler. Under dinitrogen the apparatus was charged with $C_6H_5Si(OEt)_3$ (4.12 g, 20.34 mmol), $Cr(CO)_6$ (6 g, 27.25 mmol), di-*n*-butyl ether (90 mL), and tetrahydrofuran (10 mL). The mixture was stirred and heated to a gentle reflux for 48 h. The progress of the reaction was monitored by occasionally allowing the reaction to cool to room temperature and recording the IR spectrum of the supernatant solutions. Over the course of the reaction new carbonyl bands at 1977 and 1904 cm^{-1} were observed to increase in intensity. The final mixture was cooled to room temperature and then to −10 °C for 12 h. The suspension was filtered through a pad of silanized silica (3 × 3 cm) to remove the small amounts of insoluble gray-green decomposition product and also some unreacted $Cr(CO)_6$. From the resulting yellow solution, the solvent was removed in vacuo and the residue purified chromatographically (2 × 30 cm) on silanized silica using *n*-hexane (or in some cases CH_2Cl_2/*n*-hexane (1:5 v/v) mixture) as eluent. The yellow band was collected and the solvent removed under reduced pressure. The yellow oil resulting was recrystallized from petroleum ether (40–60 °C) or *n*-hexane and cooled to −35 °C for about 48 h, to give analytically pure $\{\eta^6\text{-}C_6H_5Si(OEt)_3\}Cr(CO)_3$ (1) as yellow crystals in 70% (5.36 g, 14.24 mmol) isolated yield.

The related complexes $\{\eta^6\text{-}C_6H_5Si(OMe)_2Me\}Cr(CO)_3$ (2), $\{\eta^6\text{-}C_6H_5(CH_2)_2Si(OMe)_3\}Cr(CO)_3$ (3), $\{\eta^6\text{-1,4-}C_6H_4[(CH_2)_2Si(OMe)_3]_2\}Cr(CO)_3$ (4), $\{\eta^6\text{-}C_6H_5Si(Me)_2H\}Cr(CO)_3$ (5), $\{\eta^6\text{-1,4-}C_6H_4[Si(Me)_2H]_2\}Cr(CO)_3$ (6), and $\{\eta^6\text{-}C_6H_5Si(NMe_2)_2Me\}Cr(CO)_3$ (8) are prepared and purified in a similar fashion. Complexes 2–4 were isolated as analytically pure yellow oils.

Method B:

$$(MeCN)_3Cr(CO)_3 + (1,4\text{-}C_6H_4RR') \rightarrow (\eta^6\text{-1,4-}C_6H_4RR')Cr(CO)_3 + 3MeCN$$

$\{\eta^6\text{-}C_6H_5Si(Me)_2CH{=}CH_2\}Cr(CO)_3$ (7). Chromium hexacarbonyl (4.0 g, 18.20 mmol) was converted to $(MeCN)_3Cr(CO)_3$ in refluxing MeCN for 24 h. The mixture was allowed to cool, and the solvent was removed under reduced pressure. Recently prepared $(MeCN)_3Cr(CO)_3$ (2.50 g, 10.2 mmol) was treated with dimethylvinylphenylsilane (1.6 g, 10.2 mmol) in dry oxygen-free

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cyclohexane (60 mL) under N_2. The stirred mixture was heated gently to 65–70 °C, with IR monitoring of the course of the reaction. The heating was continued until the ν(CO) bands due to $(\text{MeCN})_3\text{Cr(CO)}_3$ had disappeared and the new ν(CO) bands at 1978 and 1912 cm^{-1} stopped increasing in intensity (24 h). The mixture was cooled to room temperature and filtered through a short column of silanized silica (3 × 3 cm). From the yellow filtrate the solvent was removed under vacuum, and the yellow residue was diluted in light petroleum ether (bp 40–60 °C) and subjected to column chromatography in silanized silica. Elution with the same solvent gives a single yellow band, which was collected, and the solvent was removed under reduced pressure, resulting in a yellow-pale orange oil. Upon cooling of the oil to −40 °C for several days, yellow crystals were formed corresponding to the desired compound $\{\eta^6\text{-C}_6\text{H}_5\text{Si(Me)}_2\text{CH{=}CH}_2\}\text{Cr(CO)}_3$ (7) in 42% (1.27 g, 4.28 mmol) yield.

Complexes $\{\eta^6\text{-1,4-C}_6\text{H}_4[(\text{CH}_2)_2\text{Si(OMe)}_3]_2\}\text{Cr(CO)}_3$ (4), $\{\eta^6\text{-C}_6\text{H}_5\text{Si(Me)}_2\text{H}\}\text{Cr(CO)}_3$ (5), and $\{\eta^6\text{-1,4-C}_6\text{H}_4[\text{Si(Me)}_2\text{H}]_2\}\text{Cr(CO)}_3$ (6) can be also prepared in a similar fashion.

Method C:

$$\{\eta^6\text{-C}_6\text{H}_5\text{Li}\}\text{Cr(CO)}_3 + \text{ClR} \xrightarrow[-78\ ^\circ\text{C}]{\text{THF}} \{\eta^6\text{-C}_6\text{H}_5\text{R}\}\text{Cr(CO)}_3 + \text{LiCl}$$

$$\{\eta^6\text{-1,4-C}_6\text{H}_4\text{Li}_2\}\text{Cr(CO)}_3 + 2\text{ClR} \xrightarrow[-78\ ^\circ\text{C}]{\text{THF}} \{\eta^6\text{-1,4-C}_6\text{H}_4\text{RR}'\}\text{Cr(CO)}_3 + 2\text{LiCl}$$

$\{\eta^6\text{-C}_6\text{H}_5\text{Si(NMe}_2)_2\text{Me}\}\text{Cr(CO)}_3$ (8). A chilled (−78 °C) THF (100 mL) solution containing $(\eta^6\text{-C}_6\text{H}_6)\text{Cr(CO)}_3$ (1.87 g, 8.73 mmol) was treated with 1 equiv of n-butyllithium (2.5 M in hexane) following the literature methods[44] and stirred for an additional 30 min. The yellow mixture is then treated with the appropriate chlorobis(dimethylamino)methylsilane. Thus, $\text{ClSi(NMe}_2)_2\text{Me}$ (2.38 g, 17.46 mmol) was cannulated into the previously generated $(\eta^6\text{-C}_6\text{H}_5\text{Li})\text{Cr(CO)}_3$ at −78 °C. The resulting mixture was stirred at −78 °C for 1 h and then allowed to warm to ambient temperature and stirred for 12 h. The yellow-orange solution was filtered through a pad of silanized silica (3 × 3 cm) and the filtrate concentrated under reduced pressure and subjected to column chromatography (2 × 30 cm) on silanized silica, as it was indicated in methods A or B. Final purification was achieved by recrystallization by diffusing n-hexane into a CH_2Cl_2 solution of the complex at −35 °C to give $\{\eta^6\text{-C}_6\text{H}_5\text{Si(NMe}_2)_2\text{Me}\}\text{Cr(CO)}_3$ (8) as a yellow crystalline material in 55% (1.65 g, 4.80 mmol) yield.

$\{\eta^6\text{-1,4-C}_6\text{H}_4[\text{Si(Me)}_2\text{H}]_2\}\text{Cr(CO)}_3$ (6). Compound $(\eta^6\text{-1,4-C}_6\text{H}_4\text{Li}_2)\text{Cr(CO)}_3$ was prepared from $\{\eta^6$-1,4-bis(tri-n-butylstannyl)benzene$\}$chromium tricarbonyl (4.0 g, 5.0 mmol) and 2.1 equiv of n-BuLi (2.5 M in hexane) in THF at −78 °C, as in ref 9. Onto this mixture a THF (10 mL) solution containing dimethylchlorosilane (1.18 g, 12.5 mmol) was cannulated, at −78 °C. The mixture was stirred at this temperature for 30 min and then permitted to warm to room temperature and stirred for 2 h. The mixture was filtered through silanized silica, and the filtrate was concentrated under reduced pressure. The crude product was subjected to column chromatography (2 × 30 cm) on silanized silica, eluting with n-hexane/benzene (9:1 v/v). The first yellow band was collected, and the solvents were removed at reduced pressure. Recrystallization as described above produced $\{\eta^6\text{-1,4-C}_6\text{H}_4[\text{Si(Me)}_2\text{H}]_2\}\text{Cr(CO)}_3$ (6) as a yellow crystalline solid in 50% (0.82 g, 2.50 mmol) yield.

Preparation of the $\{\eta^6\text{-1,4-C}_6\text{H}_4\text{RR}'\}\text{Cr(CO)}_2(\text{P(OBu)}_3)$ Complexes. All photochemical treatments of the $\{\eta^6\text{-1,4-C}_6\text{H}_4\text{RR}'\}\text{Cr(CO)}_3$ complexes 1–8 with P(OBu)_3 were performed in a similar manner. The procedure for $\{\eta^6\text{-C}_6\text{H}_5\text{Si(OEt)}_3\}\text{Cr(CO)}_2(\text{P(OBu)}_3)$ (9) is described in detail as a representative example.

A cyclohexane (75 mL) solution of 1 (0.6 g, 1.58 mmol) and tri-n-butyl phosphite (1.98 g, 7.96 mmol) was degassed with N_2 and irradiated at room temperature. The IR spectrum of the reaction was monitored after each 15-min irradiation interval. The progress of the reaction was followed by monitoring the disappearance of the A_1 ν(CO) band of the tricarbonyl complex (at 1982 cm^{-1} for 1) and the appearance of the new ν(CO) band, at 1861 cm^{-1}, corresponding to the dicarbonyl complex. Irradiation was continued until the former band had disappeared and the new CO band had reached maximum intensity (ca. 3 h). The solvent was removed under vacuum and the orange residue redissolved in the minimum volume of benzene/n-hexane (1:15 v/v) and subjected to column chromatography. The first orange band was collected, and the solvents were removed to afford pure $\{\eta^6\text{-C}_6\text{H}_5\text{Si(OEt)}_3\}\text{Cr(CO)}_2(\text{P(OBu)}_3)$ (9) as an orange oil in 55% (0.52 g, 0.869 mmol) yield. Anal. Calcd for $\text{C}_{26}\text{H}_{47}\text{O}_8\text{SiPCr}$: C, 52.12; H, 7.85. Found: C, 52.40; H, 8.01. IR (CH_2Cl_2): ν(CO) 1904, 1842 cm^{-1}.

In a similar fashion the following complexes were obtained in ca. 50–65% yield. For complexes 10, 11, 13, and 16 a further purification by column chromatography with n-hexane as eluent was effected:

$\{\eta^6\text{-C}_6\text{H}_5\text{Si(OMe)}_2\text{Me}\}\text{Cr(CO)}_2(\text{P(OBu)}_3)$ (10). Anal. Calcd for $\text{C}_{23}\text{H}_{41}\text{O}_7\text{SiPCr}$: C, 51.11; H, 7.59. Found: C, 51.86; H, 7.65.

$\{\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_2\text{Si(OMe)}_3\}\text{Cr(CO)}_2(\text{P(OBu)}_3)$ (11). Anal. Calcd for $\text{C}_{25}\text{H}_{45}\text{O}_8\text{SiPCr}$: C, 51.32; H, 7.69. Found: C, 51.96; H, 7.82.

$\{\eta^6\text{-C}_6\text{H}_4\text{-1,4-}[(\text{CH}_2)_2\text{Si(OMe)}_3]_2\}\text{Cr(CO)}_2(\text{P(OBu)}_3)$ (12). Anal. Calcd for $\text{C}_{30}\text{H}_{57}\text{O}_{11}\text{Si}_2\text{PCr}$: C, 49.07; H, 7.77. Found: C, 49.73; H, 8.03.

$\{\eta^6\text{-C}_6\text{H}_5\text{Si(Me)}_2\text{H}\}\text{Cr(CO)}_2(\text{P(OBu)}_3)$ (13). Anal. Calcd for $\text{C}_{22}\text{H}_{39}\text{O}_5\text{SiPCr}$: C, 59.25; H, 8.02. Found: C, 60.03; H, 7.97.

$\{\eta^6\text{-1,4-C}_6\text{H}_4[\text{Si(Me)}_2\text{H}]_2\}\text{Cr(CO)}_2(\text{P(OBu)}_3)$ (14). Anal. Calcd for $\text{C}_{24}\text{H}_{44}\text{O}_5\text{Si}_2\text{PCr}$: C, 55.38; H, 8.65. Found: C, 54.65; H, 8.26.

$\{\eta^6\text{-C}_6\text{H}_5\text{SiCH{=}CH}_2(\text{Me})_2\}\text{Cr(CO)}_2(\text{P(OBu)}_3)$ (15). Anal. Calcd for $\text{C}_{24}\text{H}_{41}\text{O}_5\text{SiPCr}$: C, 59.01; H, 8.40. Found: C, 59.79; H, 8.97.

$\{\eta^6\text{-C}_6\text{H}_5\text{Si(NMe}_2)_2\text{Me}\}\text{Cr(CO)}_2(\text{P(OBu)}_3)$ (16). Anal. Calcd for $\text{C}_{25}\text{H}_{47}\text{N}_2\text{O}_5\text{SiPCr}$: C, 56.17; H, 8.80; N, 5.24. Found: C, 56.65; H, 8.81; N, 5.48.

Polycondensation of $\{\eta^6$-(Bis(dimethylamino)methylsilyl)benzene$\}$chromium Tricarbonyl with 1,4-Bis(hydroxydimethylsilyl)benzene. Monomer 8 (0.80 g, 2.30 mmol) was dissolved in dried deoxygenated toluene (3 mL), in a Schlenk tube fitted with a reflux condenser and N_2 inlet. Then, recrystallized $\text{1,4-C}_6\text{H}_4[\text{Si(Me)}_2\text{OH}]_2$ (0.52 g, 2.3 mmol) was added along with 5 mL of toluene. A slight nitrogen stream was maintained, and the mixture was gently heated to 50 °C, with stirring. At this point the disilanol dissolved and dimethylamine evolution was observed. The polymerization temperature was increased to reflux and held for 1 h. Then toluene was removed at reduced pressure, also facilitating removal of Me_2NH. The viscous mixture resulting was stirred at 60 °C under vacuum for an additional 1 h. The yellow-brown oily residue was redissolved in toluene (30 mL) and filtered through a pad of silica (3 × 3 cm), and the filtered yellow toluene solution was concentrated and added dropwise to dry deoxygenated methanol (150 mL) with vigorous stirring. The solution was separated by decantation of the yellow-green gum product formed. This was reprecipitated one more time from toluene (20 mL) into methanol (100 mL). Polymer $[\text{-SiMe}\{\eta^6\text{-C}_6\text{H}_5\}\text{Cr(CO)}_3\text{OSiMe}_2(\text{1,4-C}_6\text{H}_4)\text{SiMe}_2\text{O-}]_n$ (17) was finally isolated as a thick-yellow rubberlike material, which was dried in vacuum for 24 h at 10^{-3} Torr (0.88 g).

^{1}H NMR (CDCl_3): δ 7.54 (s, 4 H, 1,4-C_6H_4), 5.42 (t, 1 H, H_p C_6H_5), 5.28 (d, 2 H, H_o, C_6H_5), 5.05 (t, 2 H, H_m, C_6H_5), 0.35 (m, H, CH_3). IR (CH_2Cl_2): ν(CO) 1970, 1982 cm^{-1}. $\bar{M}_n$ (VPO, CHCl_3): 4800 g/mol.

Homopolymerization of $\{\eta^6$-(Dimethylvinylsilyl)benzene$\}$chromium Tricarbonyl. The monomer complex 7 (0.4 g, 1.6 mmol) and AIBN (10 mg) were dissolved in dry and degassed benzene (8 mL) in a Schlenk tube, and the mixture was heated to 70 °C for 24 h. The mixture was allowed to cool to room temperature, diluted with benzene, and filtered through a pad of silica. The filtered benzene solution was concentrated and added dropwise to light-petroleum ether (40–60 °C) with stirring. The solid formed was collected by filtration, washed with additional petroleum ether, and dried under reduced pressure for 24 h. Polymer $[\text{-CH}_2\text{CH}\{\eta^6\text{-C}_6\text{H}_5\text{SiMe}_2\}\text{Cr(CO)}_3\text{-}]_n$ (18) was finally isolated as a yellow fibrous solid.

^{1}H NMR (CDCl_3): δ 5.50 (t, H, H_p, C_6H_5), 5.41 (d, 2 H, H_o, C_6H_5), 5.12 (t, 2 H, H_m, C_6H_5), 1.25 (m, H, CH_2), 0.38 (s, H, CH_3). IR (CH_2Cl_2): ν(CO) 1965, 1882 cm^{-1}. $\bar{M}_n$ (VPO, CHCl_3): 2600 g/mol.

Hydrosilylation Reactions. The reactions of 1,3-divinyltetramethyldisiloxane with both complexes 5 and 6 were performed in a similar way as described below.

Under nitrogen atmosphere, complex $\{\eta^6\text{-}C_6H_5Si(Me)_2H\}Cr(CO)_3$ (**5**) (1.04 g, 3.8 mmol) in toluene (5 mL) was added into a toluene solution (10 mL) of $(CH_2{=}CHSiMe_2)_2O$ (0.5 g, 2.7 mmol). After addition of 0.1 mL of chloroplatinic acid solution, the reaction mixture was heated to 85–90 °C. The reaction was continued until the ν(Si–H) IR band (at 2132 cm^{-1}) had disappeared. After purification by filtration on silica and precipitation with petroleum ether, the dinuclear complex $\{\eta^6\text{-}C_6H_5SiMe_2(CH_2)_2SiMe_2\text{-}\}_2O\text{-}[Cr(CO)_3]_2$ (**20**) was isolated as a yellow solid, which was dried in vacuum for 24 h (60% yield, 0.82 g, 1.14 mmol).

Anal. Calcd for $C_{32}H_{46}O_7Si_4Cr_2$: C, 49.31; H, 5.75. Found: C, 48.95; H, 5.05.

^1H NMR ($CDCl_3$): δ 5.45 (t, H_p, C_6H_5), 5.38 (d, H_o, C_6H_5), 5.11 (t, H_m, C_6H_5), 2.38, 1.50 (m, H, CH_2), 0.3 (m, H, CH_3). IR (CH_2Cl_2): ν(CO) 1970, 1966 cm^{-1}. $\bar{M}_n$ (VPO, $CHCl_3$): 675 g/mol.

Following the same method, complex **6** (1.6 g, 4.84 mmol) was treated with an excess of $(CH_2{=}CHSiMe_2)_2O$, until disappearance of the ν(Si–H) band (2118 cm^{-1}), showing that all of the starting mononuclear complex had been converted into polymer **19**. After purification as above, compound $[-SiMe_2\{\eta^6\text{-}1,4\text{-}C_6H_4\}Cr(CO)_3SiMe_2(CH_2)_2SiMe_2OSi(CH_2)_2-]_n$ was isolated as a yellow gum solid, which was dried in vacuum for 24 h.

^1H NMR ($CDCl_3$): δ 5.38 (s, H, 1,4-C_6H_4), 1.2–1.6 (m, H, CH_2), 0.4–0.2 (m, H, CH_3). IR (CH_2Cl_2): ν(CO) 1964, 1888 cm^{-1}. $\bar{M}_n$ (VPO, $CHCl_3$): 4700 g/mol.

Preparation of SiO_2-Supported $\{\eta^6$-(Alkoxysilyl)arene$\}$-$Cr(CO)_3$ Derivatives. For the attachment of complexes **1**–**4** to silica surfaces, silica gel previously treated with dry methanol under reflux was used.[46] Modification of this silica with chromium tricarbonyl species was carried out by heating a sample (3–5 mmol) of each one of the **1**–**4** derivatives with about 1 g of methanol-treated silica, in toluene suspension, under nitrogen for about 18 h. The silica material, which was now yellow, was isolated by filtration, washed several times with toluene and then with dichloromethane, and dried in vacuum at 40 °C.

The properties of the functionalized silica so obtained are described under Results and Discussion.

Studies on Polymerization of PhC≡CH Catalyzed by $\{\eta^6$-(Organosilyl)arene$\}Cr(CO)_3$. These studies were performed by following the experimental procedures previously described.[13,17]

In homogeneous conditions, solutions of phenylacetylene (4.65 g, 45.5 mmol) in benzene (10 mL) were heated in the presence of complexes **1**–**4** (ca. 0.5 mmol). In the heterogeneous procedure, PhC≡CH was treated with ca. 0.5 g of SiO_2-supported **1**–**4** complexes. From the resulting reaction mixture the SiO_2-supported catalyst was separated by filtration. The products were isolated and purified as described.

Acknowledgment. We thank the Dirección General de Investigación Científica y Técnica (DGICYT) (Proyect No. 87/0123) for financial support of this work.

Registry No. **1**, 138813-88-4; **2**, 137779-62-5; **3**, 138813-89-5; **4**, 138813-90-8; **5**, 122780-39-6; **6**, 75830-40-9; **6**$^+$, 138834-40-9; **7**, 138813-91-9; **8**, 138813-92-0; **9**, 138813-93-1; **9**$^+$, 138814-01-4; **10**, 138834-39-6; **11**, 138813-94-2; **12**, 138813-95-3; **13**, 138813-96-4; **13**$^+$, 138814-02-5; **14**, 138813-97-5; **15**, 138813-98-6; **16**, 138813-99-7; **17**, 138814-04-7; **18**, 138814-03-6; **19**, 138814-05-8; **20**, 138814-00-3; $Cr(CO)_6$, 13007-92-6; $C_6H_5Si(OEt)_3$, 780-69-8; $C_6H_5Si(OMe)_2Me$, 3027-21-2; $C_6H_5(CH_2)_2Si(OMe)_3$, 49539-88-0; 1,4-C_6H_4-$[(CH_2)_2Si(OMe)_3]_2$, 60354-74-7; $C_6H_5Si(Me)_2H$, 766-77-8; 1,4-$C_6H_4[Si(Me)_2H]_2$, 2488-01-9; $C_6H_5Si(NMe_2)_2Me$, 33567-83-8; $(MeCN)_3Cr(CO)_3$, 16800-46-7; $CH_2{=}CHSi(Me)_2H$, 18243-27-1; $ClSi(NMe_2)_2Me$, 10339-02-3; $(\eta^6\text{-}C_6H_6)Cr(CO)_3$, 12082-08-5; $(\eta^6\text{-}1,4\text{-}C_6H_4Li_2)Cr(CO)_3$, 115775-85-4; $ClSi(Me)_2H$, 1066-35-9; 1,4-$C_6H_4[Si(Me)_2OH]_2$, 2754-32-7; $(CH_2{=}CHSiMe_2)_2O$, 2627-95-4; PhC≡CH, 536-74-3; $[\{\eta^6\text{-}1,4\text{-}C_6H_4(SnBu_3)_2\}Cr(CO)_3]$, 115775-86-5; $(PhC{\equiv}CH)_n$, 25038-69-1; $P(OBu)_3$, 102-85-2.

Rearrangement, Hydride Abstraction, and Retro Ene Reactions of Dicarbonyl(η^5-cyclopentadienyl)iron Vinylidene Triflates

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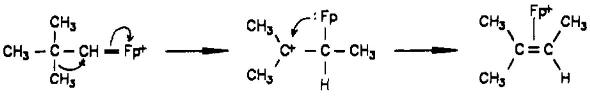
Received July 3, 1991

Several $(CO)_2CpFe$ (i.e. Fp) η^1-polymethylenevinylidene triflates, $(CH_2)_nC{=}C{=}Fp^+TfO^-$ (**3a**–**e**, n = 4–7, 10), were prepared at −78 °C from the corresponding Fp cycloalkylacyls $(CH_2)_nCHC(O)Fp$ (**1a**–**e**, n = 4–7, 10) and triflic anhydride. Solutions of **3c**–**e** in CH_2Cl_2, when warmed to 25 °C and reacted completely before being diluted with diethyl ether, are converted exclusively to Fp η^2-homocycloalkyne triflate, $\{Fp-[\eta^2\text{-}(CH_2)_n(C{\equiv}C)]\}^+TfO^-$ (**5c**–**e**, n = 7, 8, 10). This rearrangement, the organometallic analogue of an "end-to-end" alkyl shift in a vinyl cation, has not been previously observed in transition-metal vinylidenes. In contrast to **3c**–**e**, solutions of **3a,b** (and also **3c** at 0 °C) in CH_2Cl_2, when warmed to 25 °C and diluted with diethyl ether, react with the diluent to yield mixtures of Fp η^2-methylenecycloalkane triflates, $\{Fp\text{-}[\eta^2\text{-}(CH_2)_nC{=}CH_2]\}^+TfO^-$ (**9a**–**c**, n = 4–6), and Fp polymethyleneethoxycarbene triflates, $\{Fp-[\eta^1\text{-}C(OEt)CH(CH_2)_n]\}^+TfO^-$ (**12a**–**c**, n = 4–6). **9b** formed from **1b** and triflic anhydride in perdeuteriodiethyl ether contains ~1.6 atoms of deuterium per molecule, suggesting that, in the absence of a viable course of rearrangement or a better nucleophile, **3a**–**c** produce **9a**–**c** by abstracting a hydride from diethyl ether.

Dicarbonyl(η^5-cyclopentadienyl)iron (i.e. Fp) η^1-neopentylidene type complexes typically rearrange by shifting a carbon from the β- to the α-position, forming thereby a trisubstituted η^2-olefin complex (eq 1).[1] The rearrangement probably involves an intermediate carbocation.[1-3] If Fp η^1-alkylidenes are thought of as iron-sta-



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