Experimental and Theoretical Study of the Substituted (η^6-arene)Cr(CO)$_3$ Complexes

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ABSTRACT

Synthesis of arenetricarbonylchromium(0) complexes, [(η^6-arene)Cr(CO)$_3$], has been carried out, wherein arene were benzene (Ph), chlorobenzene (PhCl), phenyl trimethyl silane (PhSiMe$_3$), and acenaphthene (PhNp). Characterization of the compounds was carried out using NMR, IR and UV-visible spectrophotometers. Electronic absorption of these complexes were measured in various solvents namely methanol, methylene chloride, chloroform, benzene, and isooctane. The complexes showed the electronic absorption of the lowest in the energy range of 313-320 nm, with a relatively high intensity. Density functional theory at the B3LYP/LanL2DZ level of theory was also used to study the geometry parameters, binding energy (BE), vibrational spectra, electronic spectra, frontier molecular orbital (NBO analysis), charge transfer (CT) of the complexes. It was found that the order of the complex stability is: (PhSiMe$_3$)Cr(CO)$_3$> (Ph)Cr(CO)$_3$> (PhNp)Cr(CO)$_3$> (PhCl)Cr(CO)$_3$. The NBO analysis showed that the stability of the complexes arising from intramolecular interactions and electron delocalization in which synergistic interaction occurs in the arene hyper conjugative orbital ring for metal antibonding orbital and back donation (via metal bonding orbital to bond antibonding orbital ring). The electronic spectrum shows the charge transfer is dominated by ligand to metal charge transfer (LMCT) transition, except for (PhNpe) Cr(CO)$_3$that is dominated by metal to ligand charge transfer (MLCT) and only a small portion is set to d-d transition.

Keywords: Arenetricarbonylchromium, Charge transfer transition, DFT, TD-DFT, NBO.

INTRODUCTION

Arene chromium tricarbonyl compounds have been explored extensively and are very versatile agents[1-9]. This compound has many applications ranging from organic synthesis, molecular switches, tunable molecular cables, optical information storage devices and nonlinear optical materials[10-12]. Many earlier studies have explored preparation of arena chromium tricarbonyl compounds, yet, their syntheses remain an ongoing challenge. The presence of electron withdrawing substituent on the benzene ring deflects π-electron density of the arene, therefore the arene fails to react

with the chromium hexacarbonyl; several arenes with electron withdrawing substituentsdo not undergo complexation, e.g. benzoic acid, benzaldehyde, nitrobenzene and benzonitrile[13].

The polysubstituted complex reported in this paper are (benzene)$Cr(CO)_3$, (chlorobenzene) $Cr(CO)_3$, (acenaphthene) $Cr(CO)_3$, and (phenyltrimethylsilane)$Cr(CO)_3$. Earlier study explored the nature of the lowest excited states of these complexes, in which it was reported that the lowest absorption energy band consist with a mixture of ligand field (LF) and metal to arene charge transfer (MArCT) transitions[14]. Unfortunately, the definite order of these transitions could not be resolved well experimentally. This study reported the synthesis and quantum chemical study of polysubstituted (η^6-arene) $Cr(CO)_3$complexes. The quantum chemical study includes geometry molecules, electronic populations and electronic structures of the complexes. The theoretical analysis was performed for optimized molecular geometry, frontier molecular orbital by using the natural bond orbitals scheme, vibrational frequencies, and electronic absorption spectra. The latter was used to identify the nature of the interactions between metal and the ligands in terms of the intensity of metal to ligand or ligand to metal charge transfer (MLCT/LLCT). The electronic absorption spectra were calculated by time dependent density functional theory (TD-DFT) to interpret the UV–Vis spectra obtained at an experimental level.

EXPERIMENTAL

All reagents were commercially available and were used without further purification.

Synthesis

In general, the chromium tricarbonyl complexes were synthesized by refluxing the same amount of moles of chromium hexacarbonyl and appropriate aromatic ligands in aninert solvent for 9 - 48 hours depending on the arene ligands. The mixtures were then filtered using alumina column, followed by rotatory evaporation, and recrystallization. The complexes are obtained in the form of robust solids which have the color ranging from yellow to orange. They are relatively stable in air at room temperature.

Physical measurements

The infrared spectra were recorded on a Perkin-Elmer 283B spectrophotometer using KBr pellet. Electronic spectra were measured on UV-Vis (HP 8450A) spectrophotometer in methanol, benzene, chloroform, dichloromethane, and iso octane solution. ^{1}H NMR spectra were obtained at room temperature in $CDCl_3$ using a Bruker AM 360 spectrometer.

Computational Method

All calculations have been performed with the GAUSSIAN-03 program[15]. Geometry optimizations utilized the B3LYP method[16-18] and the LANL2DZ basis set[19]. Previous studies have shown this to be an appropriate level of theory for chromium tricarbonyl complex of arenes[20-21]. NBO[22-24] calculations have been done at B3LYP/ LANL2DZ level.
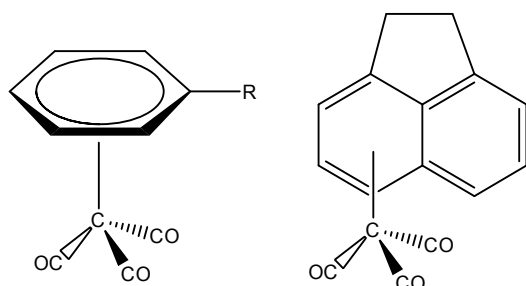
RESULTS and DISCUSSION

The structures of arene chromium tricarbonyl complexes were optimized at the density functional level of theory using the B3LYP/LanL2DZ methodology. The different types of substituents were added into the benzene unit as depicted in Scheme 1. Figure 1 depicts the mode of substitution of the benzene unit, which was performed with all of the aforementioned moieties.
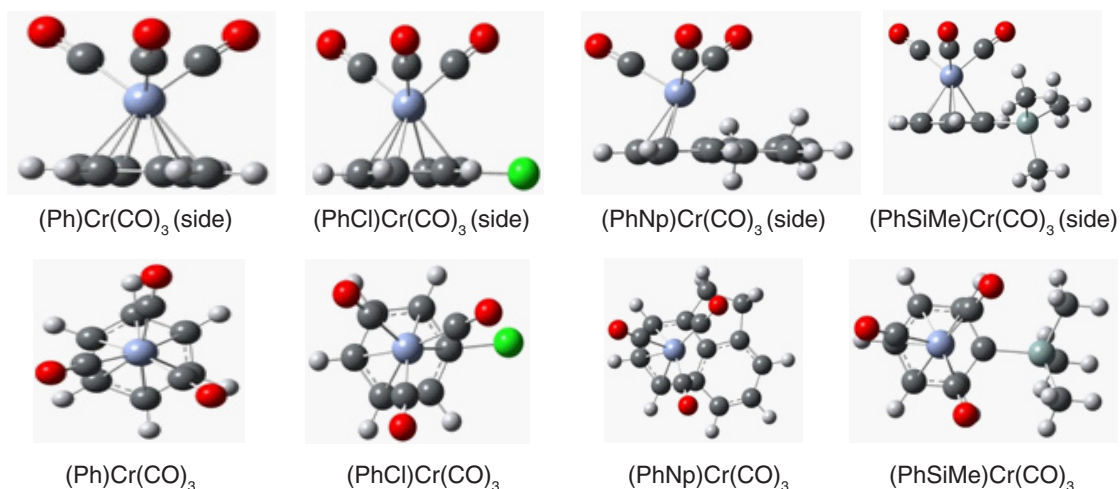
The geometrical properties of the complexes show that the structural changes in (η^6-arene)$Cr(CO)_3$ complex induced by introducing different substituent groups is very small (Fig. 1) owing to the tripod C-O bonds making the molecule rigid. This leads to a small number of conformational isomers, and as a result the computational effort is also reduced. The calculated geometry is in a good agreement with the X-ray structural measurements of (Ph) $Cr(CO)_3$. The calculated Cr-O bond distances for all complexes are relatively similar range from 1.8293 Å to 1.8386 Å. In the complex of (PhNp)$Cr(CO)_3$ the position of $Cr(CO)_3$ tripod 0.17 Å shifts from the ring center toward the most external C-C bond (parallel to the bond between the two rings). The distance of chromium to the ring center for (PhNp)$Cr(CO)_3$ is about 1.80 Å, a slightly longer distance compared to benzene-Cr interaction at (Ph)$Cr(CO)_3$ of 1.720 Å (exp.: 1.724-1.726 Å)[25].

Hexacarbonylchromium(0), $Cr(CO)_6$, is a reactant in the synthesis of (arene)$Cr(CO)_3$ complexes. In the $Cr(CO)_6$ molecule, Cr-C-O bond has a linear shape and structure of the Cr-C-O can easily be identified on the IR spectrum that showed CO stretching mode in the 1850-2125 cm^{-1} [26]. The unique identity of (arene)$Cr(CO)_3$ is the presence of two high-intensity IR absorption which are stretching modes of COligand; the energy absorptions are in the area 2000 - 1960 cm^{-1}, and in the area of energy from 1910 to 1870 cm^{-1}. Assuming C_{3v} symmetry locally on the cluster of $Cr(CO)_3$, the two uptakes is thought to originate from vibrations of symmetric non degenerate (A_1) and antisymmetric double degenerate (E) [27]. IR spectra and ^{1}HNMR spectra for all of four chromium tricarbonyl complexes are presented in Table 1.

X-ray crystallography and neutron diffraction[28] concluded that the C - C in the arene ring elongated compared to its native form (prior coordinated with the group $Cr(CO)_3$. This phenomenon is interpreted as a form of a reduction in the degree of aromaticity of the ring of arene after coordination with chromium group of tricarbonyl[29]; an explanation that is consistent with the results of ^{1}HNMR spectra in this study. Interaction of $Cr(CO)_3$ with the arene ring reduce selectron density in the ring[30]. This results in lower degrees of aromaticity, manifested in the ^{1}HNMR spectra that indicate the presence of hydrogen aromatic shift into a higher energy position (up field) (δ = 4.6 to 5.6 ppm, while the free aromatic ranging from 6.0 to 7.0 ppm).

A characteristic feature of electronic absorptions of arenetricarbonylchromium(0) complexes is the maximum absorption in the region 313-320 nm with high intensity ($\varepsilon \sim 0.97 \times 10^4$ up to 2.04×10^4 $M^{-1}cm^{-1}$), except for (PhNp)$Cr(CO)_3$ complex that has λ_{max} at 352 nm with an intensity that is almost the same ($\varepsilon \sim 0.91 \times 10^4$ $M^{-1}cm^{-1}$). This indicates a transition from metal to ligand and ligand to metal charge transfers (MLCT/LMCT).

In order to assign the already reported experimental electronic absorption bands of (Ph)$Cr(CO)_3$, (PhCl)$Cr(CO)_3$, (PhNp)$Cr(CO)_3$, and (PhSiMe)$Cr(CO)_3$, the TD-DFT calculations have been carried out on these complexes in methanol at the B3LYP/GEN level of theory. TD-DFT is a useful method for studying excitation energies, and its application has increased in the recent years[31].

Scheme 1: Molecular structure of the studied polysubstituted (η^6-arene)$Cr(CO)_3$ complexes

(Ph)$Cr(CO)_3$ (side)   (PhCl)$Cr(CO)_3$ (side)   (PhNp)$Cr(CO)_3$ (side)   (PhSiMe)$Cr(CO)_3$ (side)

(Ph)$Cr(CO)_3$ (PhCl)$Cr(CO)_3$ (PhNp)$Cr(CO)_3$ (PhSiMe)$Cr(CO)_3$

Fig. 1: Two projections of the fully optimized structures of (η^6-arene)-$Cr(CO)_3$ complexes at B3LYP level of theory

This method does give some errors in the excitation energies of charge-transfer states, however; better results may be obtained by using hybrid functionals which include a mixture of exact Hartree-Fock exchange with DFT exchange correlation[32]. The calculated electronic excitation energies and transition wavelengths (λ_{cal}) of the complexes, along with their oscillator strengths, assignments

and transitions with significant coefficients of the wave function are listed in Table 4, along with the experimental transition wavelengths (λ_{exp}).

Transition metal complexes generally show three types of electronic excitation bands that cover a wide wavelength range: d-d (crystal-field) transitions (300 - 1500 nm); metal-to-ligand charge-transfer (MLCT) and ligand-to-metal charge transfer (LMCT) transitions (200 - 500 nm); transitions that are localized on the ligands commonly known as intra-ligand charge transfer (ILCT) transitions, that regularly occur in the ultraviolet region[33]. ILCT results from $n \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions and are affected by the type of coordination.

The scaling factor 0.72 was used to correct the calculated singlet-singlet electronic excitation wavelengths[34]. The calculate electronic spectrum of $(Ph)Cr(CO)_3$, $(PhCl)Cr(CO)_3$, and $(PhSiMe_3)$ $Cr(CO)_3$ have closely similar bands, between 325-360 nm, that can be attributed mainly to ligand to metal charge transfer transitions and smaller band with low oscillator strength (f < 0.0005), that is due to a d-d transition. The latter assignment was made since d-d transitions usually have very low intensities and lack of solvent dependent. For $((PhNp))Cr(CO)_3$ complex, the band at 426 nm with oscillator strength

Table 1: Geometric parameters of the fully optimized structures of (η^6-arene)Cr(CO)$_3$ complexes at B3LYP level of theory

Geometrical Parameters Bond Length (A)	(Ph) Cr(CO)$_3$	(PhCl) Cr(CO)$_3$	(PhNp) Cr(CO)$_3$	(PhSiMe$_3$) Cr(CO)$_3$
Cr-O12(10)	1.8333	1.8386	1.8265	1.8281
Cr-O13(11)	1.8354	1.8354	1.8314	1.8293
Cr-O14(12)	1.8386	1.8339	1.8203	1.8304
Cr-C1	2.3183	2.3183	2.353	2.3015
Cr-C2	2.3172	2.3172	2.4035	2.3469
Cr-C3	2.3281	2.3281	2.4586	2.3027
Cr-C4	2.2985	2.2985	2.3266	2.326
Cr-C5	2.3124	2.3124	2.2842	2.3188
Cr-C6	2.298	2.298	2.3269	2.3243

Table 2: Experimented and calculated ^{1}H NMR and IR spectra of the (η^6-arene)Cr(CO)$_3$complexes

Complexes	^{1}H-NMR, δ (ppm)^a		IR, $_{CO}$, cm^{-1} (lit)^b	
	H aromatic	H substituent	A$_1$	E
(Ph)Cr(CO)$_3$	5,4 (s)	"-"	1965 (1974)^d**(1939)^f**	1887 (1898) **(1878)^f**
(PhCl)Cr(CO)$_3$	5,4 – 5,5 (m)	"-"	1980 (1992)^e**(1947)^f**	1922 (1931)^e**(1981)^f**
(PhNp)Cr(CO)$_3$	7,3 – 7,7 (m)	3,4 (s)	1968 **(1928)^f**	1871 **(1868)^f**
(PhSiMe)Cr(CO)$_3$	5,2 – 5,6 (m)	0,3 (s)	1980 **(1934)^f**	1904 **(1875)**

a) The spectra were taken in CDCl$_3$ solution; using TMS as an internal
   standard; (s) = singlet, (m) = multiplet
b) Stretching frequencies of CO relative to polystyrene. Using solvents CDCl$_3$
d) In CHCl$_3$[30]
e) In cyclohexane [30]
f) Calculated IR spectra

of 0.0240, is the most intense and attributed to electronic excitation from HOMO-2 to LUMO. This band, therefore, arises from a mixed of MLCT and LMCT charge transfer character.

In general, the binding energy is related to the stability of the complexes. The binding energies for the chromium-arene complexes were calculated as the energy difference between the complexes and their monomer. The calculated binding energies for the complexes are listed in Table 5.

The calculated binding energy of the complex are 48.73 kcal.mol^{-1}, 45.64 kcal.mol^{-1}, 45.62 kcal.mol^{-1}, and 41.46 kcal.mol^{-1} for (PhSiMe$_3$) Cr(CO)$_3$, (Ph)Cr(CO)$_3$, (PhNp)Cr(CO)$_3$, (PhCl) Cr(CO)$_3$, respectively. The (Ph)Cr(CO)3 binding energy is 45.64 kcal.mol-1, not too far from the

Table 3: Electronic absorbtion data of (η^6-arene)Cr(CO)$_3$complexes in a variety of solvent-saturated N$_2$ at 298 K

Complexes	Absorbance maximum (λ_{max}, nm)				
	CH$_3$OH	CH$_2$Cl$_2$	CHCl$_3$	C$_6$H$_6$	C$_8$H$_{18}$
(Ph)Cr(CO)$_3$	312	313	315	313	313
(PhCl)Cr(CO)$_3$	320	319	320	320	318
(PhNp)Cr(CO)$_3$	344	347	350	352	353
(PhSiMe$_3$)Cr(CO)$_3$	315	316	318	316	316

Table 4: Caculation of electronic absorptions of (Ph)Cr(CO)$_3$, (PhCl)Cr(CO)$_3$, (PhNp)Cr(CO)$_3$, and (PhSiMe$_3$)Cr(CO)$_3$complexes, in methanol, from TD-DFT calculations at the B3LYP/LanL2DZ.

Complexes	Electronic transition	Transition Coefficient (c)	Weight % of Transition	Oscillator Strength	Excitation Energy	λ_{cal}	scaled λ_{cal}	λ_{exp}	Assignment
(Ph)Cr(CO)$_3$	H →L	0.471	22.2	0.0001	3.288	377	271		MCT/ILCT
	H → L+3	0.387	15.01	0.0007	3.363	368	265		d-d/MLCT/LMCT /LLCT/ILCT
	H → L+3	0.185	3.42	0.0051	3.446	359	259	312	LMCT/ILCT
(PhCl)Cr(CO)$_3$	H → L	-0.23	5.09	0.0002	3.227	384	276		LMCT/ILCT
	H-2→ L+2	0.384	14.75	0.0043	3.290	360	259	320	LMCT/ILCT
	H-1→ L	-0.240	5.53	0.0000					d-d/MLCT/LMCT /LLCT/ILCT
	H-1→ L	0.374	13.97	0.0009	3.688	336	242		d-d/MLCT/LMCT /LLCT/ILCT
(PhNp)Cr(CO)$_3$	H→ L	0.617	38.02	0.0056	2.736	453	326		LMCT/ILCT
	H-2→ L	0.559	31.27	0.0240	2.906	426	307	344	MLCT /LMCT /ILCT
	H → L+2	0.474	22.50	0.0074	3.390	365	263		LMCT/ILCT
(PhSiMe$_3$)Cr(CO)$_3$	H-1 → L+2	0.421	17.74	0.0001	3.297	376	270		LMCT/ILCT
	H-1 → L+1	0.591	34.90	0.0030	3.632	341	245	315	LMCT/ILCT
	H-2 → L+2	0.273	7.44	0.0000					d-d/MLCT/LMCT /LLCT/ILCT
	H → L	0.288	8.29	0.0002	3.809	325	234		LMCT/ILCT

Table 5: Calculated binding energy (BE), selected second order binding energy (E2), frontier molecular orbital (HOMO-LUMO), and charge transfer (CT) of (η^6-arene)Cr(CO)$_3$complexes.

Systems	BE (kcal.mol^{-1})	E2 (kcal)		E_{HOMO} (a.u)	E_{LUMO} (a.u)	Mulliken CT (Ring→Cr)
		Ring→Cr-CO	Cr-O → Ring			
(Ph)Cr(CO)$_3$	-45.64 (43)*	199.48	15.64	-0.2213	-0.0584	0.167
(PhCl)Cr(CO)$_3$	-41.46	199.28	15.36	-0.2109	-0.0773	0.133
(PhNp)Cr(CO)$_3$	-45.62	151.35	16.66	-0.2284	-0.0687	0.135
(PhSiMe$_3$)Cr(CO)$_3$	-48.72	202.33	16.72	-0.2175	-0.0562	0.195

*Experimental value [35].

experimental value (43 kcal.mol-1) as reported by Brown *et al..* The binding energy trend shows that electron withdrawing substituent on the ring reduces the binding energies from the initial (Ph)Cr(CO)$_3$. In contrast, the presence of additional two benzene rings on (PhNp)Cr(CO)$_3$acts as electron donating groups, and therefore the binding energy increase compared to (Ph)Cr(CO)$_3$ binding energy. The binding energy trend is consistent with calculated Mulliken charge transfer trend from ring → Cr.

The stability trend of the complexes is further studied by the second-order binding energies (E2) trend based on the natural bond orbital (NBO) analysis. E2 corresponds to the intensity of interaction between Lewis donor and non-Lewis acceptor NBO[30-32, 36,37]. Table 5 shows a positive correlation of the binding energy with the second-order binding energy. All the complexes have either the bonding (ring '! σ*Cr–CO) (or) back bonding (Cr–CO → ring) interactions. The maximum E2 contribution of ring → σ*Cr–CO for(PhSiMe$_3$)Cr(CO)$_3$, (Ph)Cr(CO)$_3$, (PhCl) Cr(CO)$_3$range from 199.28-202.33 kcal with Cr–CO → ringback bonding15.64-16.72 kcal. The difference was found for ring → σ*Cr–COE2 maximum of (PhNp)Cr(CO)$_3$ complex (151.35 kcal), where two additional benzene on ligand (acenapthene) may distort interaction between Lewis donor and non-Lewis acceptor NBO.

CONCLUSION

The aim of this study was to synthesize tricarbonylchromium(0) arene complexes and to analyze synthesis products using experimental and theory studies. Synthesis products of tricarbonylchromium (0) arene complexes were (Ph)Cr(CO)$_3$, (PhCl)Cr(CO)$_3$, (PhSiMe$_3$)Cr(CO)$_3$, and (PhNp)Cr(CO)$_3$. Characterization by ^{1}H-NMR, IR, and UV-visible show that the complexes were successfully synthesized. DFT study at B3LYP/ LanL2DZ level of theory was also used to study the geometry parameters, binding energy (BE), the frontier molecular orbital (NBO analysis), the charge transfer (CT), electronic and vibration spectrum. The electronic spectrum shows the transfer fee is dominated by metal to ligand charge transfer (LMCT) transition, except (PhNp)Cr(CO)$_3$ is dominated by metal to ligand charge transfer (MLCT) and only a small portion is set to d-d transition. It was found that the complex stability order were (PhSiMe$_3$)Cr(CO)$_3$> (Ph)Cr(CO)$_3$> (PhNp)Cr(CO)$_3$> (PhCl)Cr(CO)$_3$. NBO analysis showed that the stability of the complexes arising from hyperconjugative orbital rings for metal antibonding orbital donation and back bonding orbital.

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