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THE REVERSIBLE ONE-ELECTRON OXIDATION OF ARENECHROMIUM-DICARBONYLACETYLENE COMPLEXES

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Summary

$(C_6Me_{6-n}H_n)Cr(CO)_2$(acetylene), n = 0 and 1; acetylene = PhC≡CPh and p-$MeOC_6H_4C{\equiv}CC_6H_4OMe$, are reversibly oxidised to the corresponding monocations by NO^+, Ag^+ or I_2. Electrochemical data for the oxidation process, and the ESR spectra of the resulting cations, are reported.

Introduction

In our studies of the reactions between NO^+ and (arene)$Cr(CO)_2$L derivatives, L = CO, phosphines, etc. [1, 2] we have reported preliminary results which suggested that when L was an acetylene, protonation occurs in methanol/toluene mixtures to afford $[H(arene)Cr(CO)_2(acetylene)]^+$. As well as microanalytical data for the cations, and the observation that their infra-red spectra in the carbonyl region showed shifts to higher wavenumber in comparison to the neutral starting materials, studies by other workers have shown that protonation of (arene)$Cr(CO)_2$L, L = CO and PPh_3, does occur in CF_3CO_2H [3, 4]. We have now, however, completed our studies on the acetylene complexes and have shown, by further chemical studies as well as by electrochemical and ESR experiments, that NO^+ salts in methanol/toluene or in dichloromethane afford $[(arene)Cr(CO)_2(acetylene)]^+$ by a reversible oxidation process and that protonation does not occur.

Results and discussion

In methanol/toluene mixtures either $NOPF_6$ or $AgPF_6$ react with $(C_6Me_{6-n}H_n)Cr(CO)_2(PhC{\equiv}CPh)$, n = 0 and 1, to afford maroon, crystalline precipitates of $[(C_6Me_{6-n}H_n)Cr(CO)_2(PhC{\equiv}CPh)]PF_6$. The products are analytically pure

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but may be recrystallised from $CHCl_3$/hexane or CH_2Cl_2/hexane to afford solvated species such as $[(C_6Me_6)Cr(CO)_2(PhC{\equiv}CPh)]PF_6 \cdot CHCl_3$. The infra-red spectra of the solvates are identical in the carbonyl region to those of the unsolvated complexes. The salts are air-stable, dissolving in polar solvents such as acetone, CH_2Cl_2 and $CHCl_3$ to give deep red-brown solutions which decompose in air. Addition of iodine to CH_2Cl_2 solutions of $(C_6Me_{6-n}H_n)Cr(CO)_2(PhC{\equiv}CPh)$ also results in generation of the corresponding cations. The iodide salts have not been isolated but were identified by their infra-red carbonyl spectra.

Reaction of $NOPF_6$ with other acetylene derivatives leads to the formation of similar monocations, although other products are eventually formed. In methanol/toluene $[(C_6Me_{6-n}H_n)Cr(CO)_2(p\text{-}MeOC_6H_4C{\equiv}CC_6H_4OMe)]PF_6$, $n = 0$ and 1, may be isolated as impure precipitates but attempted recrystallisation leads to decomposition. Monitoring by infra-red spectroscopy shows that these species may also be generated in CH_2Cl_2. On prolonged contact with the nitrosonium ion, however, the deep red-brown colour of solutions of the cations rapidly changes to an intense royal blue, followed by gradual formation of pale yellow $[(C_6Me_{6-n}H_n)Cr(CO)_2(NO)]PF_6$ [1]. The nature of the blue solution is unknown. It is extremely unstable in air although attempts to record its infra-red spectrum resulted in an indication that some carbonyl-containing species, other than those characterised, is present.

The monocation $[(C_6Me_5H)Cr(CO)_2(MeCO_2C{\equiv}CCO_2Me)]^+$ has not been observed; reaction of the neutral complex with $NOPF_6$ in MeOH/toluene rapidly affords $[(C_6Me_5H)Cr(CO)_2(NO)]PF_6$ and the free acetylene. However, in the light of the results from the other acetylene complexes it is likely that initial oxidation takes place followed by further reaction with excess $NOPF_6$ present, or with NO gas generated in the redox process, to form the nitrosyl-containing cation.

Apart from the observation that the carbonyl stretching frequencies for the cations are some 100—150 cm^{-1} higher than those of the neutral compounds (see Table 1), the nature of the cations has been verified by electrochemical and ESR spectral studies. In dichloromethane, cyclic voltammetry shows that each acetylene complex $(C_6Me_{6-n}H_n)Cr(CO)_2L$, $n = 0$ and 1; L = $PhC{\equiv}CPh$ and $p\text{-}MeOC_6H_4C{\equiv}CC_6H_4OMe$, undergoes a reversible one-electron oxidation reaction (Table 1) followed by an irreversible electrochemical reaction at slightly more positive potentials. It is possible that the irreversible step is loss of acetylene, as is the case for the chemical reactions described above.

The substituent effects on the oxidation potentials are as expected. The donating methoxy group in the dianisylacetylene reduces the potential for the oxidation by about 60 mV in both arene complexes studied, and the small shift to more positive potentials on substitution of C_6Me_5H for C_6Me_6 is as found by other workers in studies on the parent complexes $(arene)Cr(CO)_3$ [5]. The considerable shift of about 0.8 V to more negative potentials on substitution of one carbonyl ligand in $(arene)Cr(CO)_3$ by an acetylene is a reflection of the better σ-donor/poorer π-acceptor nature of the acetylene in comparison to the carbonyl ligand.

$[(C_6Me_{6-n}H_n)Cr(CO)_2(PhC{\equiv}CPh)]^+$, $n = 0$ and 1, and $[(C_6Me_6)Cr(CO)_2\text{-}(p\text{-}MeOC_6H_4C{\equiv}CC_6H_4OMe)]^+$ have been characterised by their room temperature ESR spectra in CH_2Cl_2. The spectra of the three species are virtually identical,

TABLE 1

INFRARED AND ELECTROCHEMICAL DATA FOR ARENECHROMIUMDICARBONYLACETYLENE COMPLEXES

Complex	ν(CO) (cm^{-1}) ^{a}	Electrochemical data			
		E_p (volts)	$(E_p)_c-(E_p)_a$ (mV)	$(i_p)_c$ (μA)	$(i_p)_a$ (μA)
$(C_6Me_6)Cr(CO)_2(C_6H_5C{\equiv}CC_6H_5)$	1900, 1821	−0.22	195	3.3	2.7
$[(C_6Me_6)Cr(CO)_2(C_6H_5C{\equiv}CC_6H_5)]PF_6$	2023, 1975	b			
$(C_6Me_5H)Cr(CO)_2(C_6H_5C{\equiv}CC_6H_5)$	1900, 1823	−0.21	175	3.4	3.1
$[(C_6Me_5H)Cr(CO)_2(C_6H_5C{\equiv}CC_6H_5)]PF_6$	2024, 1974	b			
$(C_6Me_6)Cr(CO)_2(p\text{-}MeOC_6H_4C{\equiv}CC_6H_4OMe)$	1889, 1811	−0.29	155	2.7	2.9
$[(C_6Me_6)Cr(CO)_2(p\text{-}MeOC_6H_4C{\equiv}CC_6H_4OMe)]PF_6$	2011, 1965	b			
$(C_6Me_5H)Cr(CO)_2(p\text{-}MeOC_6H_4C{\equiv}CC_6H_4OMe)$	1897, 1817	−0.27	195	2.5	2.1
$[(C_6Me_5H)Cr(CO)_2(p\text{-}MeOC_6H_4C{\equiv}CC_6H_4OMe)]PF_6$	2015, 1969	b			
$(C_6Me_5H)Cr(CO)_2(MeCO_2C{\equiv}CCO_2Me)$	1937, 1861	b			
$[Ph_4P]_2[NiS_4C_4(CN)_4]$		0.07	150	2.4	2.5

^{a} In CH_2Cl_2. ^{b} Not measured.

each exhibiting four lines due to ^{53}Cr (I 3/2; abundance 9.5%) hyperfine coupling with $\langle A_{Cr} \rangle$ equal to 15 Gauss. A single line, due to the presence of chromium isotopes with $I = 0$, is superimposed on the quartet at $\langle g \rangle$ 1.99. Although few paramagnetic organochromium complexes are known the ESR parameters for the acetylene derivatives described are in accord with those observed for $[(C_6H_6)_2Cr]^+$, ($\langle A_{Cr} \rangle \approx$ 20G; g 1.98) [6].

Experimental

All reactions described were carried out under nitrogen using dried, redistilled solvents. The (arene)Cr(CO)$_3$ complexes used in this work were prepared by standard methods [7]; the acetylene derivatives were synthesised using modifications of published procedures [8]. $NOPF_6$ and $AgPF_6$ were purchased from Ozark Mahoning Co. Ltd., Tulsa, Oklahoma.

X-band ESR spectra, calibrated against a solid sample of the diphenylpicrylhydrazyl radical, dpph, were recorded on a Varian Associates 4502/15 instrument, and infra-red spectra on a Perkin—Elmer PE257 spectrometer. Electrochemical measurements were recorded on a Beckman Electroscan 30. For the cyclic voltammetric studies the working electrode was a stationary platinum wire; the reference electrode was the saturated calomel electrode 1M in lithium chloride. Samples were prepared 10^{-3} M in CH_2Cl_2 which was also 0.05 M in $[Et_4N]ClO_4$ as the base electrolyte. Electrochemical results are quoted in comparison with those of the first oxidation wave of $[Ph_4P]_2[NiS_4C_4(CN)_4]$, known to be a reversible one-electron process.

$(C_6Me_6)Cr(CO)_2(p\text{-}MeOC_6H_4C{\equiv}CC_6H_4OMe)$

1.0 g of $(C_6Me_6)Cr(CO)_3$ and 1.0 g of p-$MeOC_6H_4C{\equiv}CC_6H_4OMe$ were dissolved in 100 ml THF and irradiated for 23 h. Filtration afforded 1.0 g of red crystals of the product. A further 0.1 g was gained by addition of 100 ml ether to the mother liquor. [Yield 57% based on $(C_6Me_6)Cr(CO)_3$.] The complex is stable in air but red solutions in solvents such as CH_2Cl_2 or acetone decompose in air.

The other acetylene complexes used in this study were prepared similarly. They appear less stable in the solid state than the species described, (C_6Me_5H)-$Cr(CO)_2(p\text{-}MeOC_6H_4C{\equiv}CC_6H_4OMe)$ being particularly prone to decomposition.

$[(C_6Me_6)Cr(CO)_2(PhC{\equiv}CPh)]PF_6$

To 0.2 g $(C_6Me_6)Cr(CO)_2(PhC{\equiv}CPh)$ suspended in a mixture of 15 ml toluene and 3 ml methanol was added 0.17 g of solid $NOPF_6$. A dark maroon solid was formed and gas was evolved. Filtration yielded 0.11 g of crystalline $[(C_6Me_6)$·$Cr(CO)_2(PhC{\equiv}CPh)]PF_6$. [Yield 42% based on $(C_6Me_6)Cr(CO)_2(PhC{\equiv}CPh)$]. Analysis found: C, 55.8; H, 4.8; N, 0.0. Calcd.: C, 56.6; H, 4.8; N, 0.0%. Recrystallisation of the salt from $CHCl_3$/hexane afforded black needles of $[(C_6Me_6)Cr$-$(CO)_2(PhC{\equiv}CPh)]PF_6 \cdot CHCl_3$. Analysis found: C, 48.4; H, 4.2; N, 0.0. Calcd.: C, 48.2; H, 4.3; N, 0.0%.

The complex is soluble in polar solvents such as acetone and CH_2Cl_2 to afford deep red-brown solutions which slowly decompose in air.

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