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Preliminary communication

THE REACTION OF ARYLDIAZONIUM SALTS WITH GROUP VI ARENE-METAL TRICARBONYL DERIVATIVES

NEIL G. CONNELLY* and ZENON DEMIDOWICZ

Department of Inorganic Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS (Great Britain)

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Summary

Diamagnetic $[(C_6Me_6)Cr(CO)_2(p\text{-}RC_6H_4N_2)]^+$ (R = H, OMe and NO_2) which react with H^- to afford neutral cyclohexadienyls, result from the reaction of $(C_6Me_6)Cr(CO)_2L$, L = CO, with diazonium salts, whereas paramagnetic $[(C_6Me_6)Cr(CO)_2(PPh_3)]^+$ results when L = PPh_3.

In conjunction with our studies of the interaction of NO^+ with (arene)Cr-$(CO)_2L$ (L = CO, phosphines, acetylenes, etc.) [1, 2] we have carried out analogous reactions with diazonium salts. In CH_2Cl_2, $[p\text{-}RC_6H_4N_2]X$ (R = H, X = PF_6; R = OMe and NO_2, X = BF_4) and $(C_6Me_6)Cr(CO)_3$ afford $[(C_6Me_6)Cr(CO)_2(p\text{-}RC_6H_4N_2)]X$ as stable, maroon crystalline solids which have been characterised by elemental analysis and NMR spectroscopy [e.g. R = NO_2, ^1H NMR: τ 7.47 (18H, s), 2.32 (2H, d, 9Hz), 1.55 (2H, d, 9Hz)]. They are the first examples of arylazochromium derivatives to be reported and are also rare examples of organometallic species. In agreement with the observation [3] that the $[p\text{-}RC_6H_4N_2]^+$ ligand is a poorer π-acceptor than NO^+, the carbonyl stretching frequencies (Table 1) of the new salts are at lower wavenumber than those of $[(C_6Me_6)Cr(CO)_2(NO)]PF_6$ [1].

In contrast to the nitrosyl complex two sites in $[(C_6Me_6)Cr(CO)_2(p\text{-}RC_6H_4N_2)]^+$, at the arene ring and at the arylazo ligand, might be expected to be susceptible to nucleophilic attack. In THF, hydride ion, from $NaBH_4$, preferentially adds to the arene ligand to afford neutral cyclohexadienyl derivatives, such as $(C_6Me_6H)Cr(CO)_2(p\text{-}NO_2C_6H_4N_2)$, [$^1H$ NMR: τ 9.05 (3H, d, 9Hz), 8.65 (6H, s), 8.40 (6H, s), 7.83 (3H, s), 3.05 (2H, d, 9Hz), 2.12 (2H, d, 9Hz), *exo*-proton obscured by methyl resonances] as stable, deep purple-brown solids. $(C_6Me_6)Cr(CO)_2(p\text{-}RC_6H_4N{=}NH)$ has not been observed although platinum diimine complexes have been prepared from the corresponding arylazo derivatives [4, 5].

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*Author to whom correspondence should be addressed.

TABLE 1

INFRARED DATA FOR ARENECHROMIUM DERIVATIVES

Complex	ν(CO) (cm^{-1})^a	ν(NN) (cm^{-1})
$(C_6Me_6)Cr(CO)_3$	1945, 1857	—
$(C_6Me_6)Cr(CO)_2(PPh_3)$	1857, 1793	—
$[(C_6Me_6)Cr(CO)_2(PPh_3)]PF_6$	1973, 1853	—
$[(C_6Me_6)Cr(CO)_2(C_6H_5N_2)]PF_6$	2025, 1977	1697
$[(C_6Me_6)Cr(CO)_2(p\text{-}MeOC_6H_4N_2)]BF_4$	2021, 1973	1701
$[(C_6Me_6)Cr(CO)_2(p\text{-}NO_2C_6H_4N_2)]BF_4$	2037, 1989	1677
$(C_6Me_6H)Cr(CO)_2(p\text{-}NO_2C_6H_4N_2)$	1989, 1941 ^{b}	—

^{a} In CH_2Cl_2 unless otherwise stated. ^{b} Hexane.

Although NO^+ substitutes either one carbonyl or the phosphine ligand on reaction with $(C_6Me_6)Cr(CO)_2(PPh_3)$ [1], $[p\text{-}RC_6H_4N_2]^+$ affords the yellow, paramagnetic cation $[(C_6Me_6)Cr(CO)_2(PPh_3)]^+$. Presumably, in functioning as a novel oxidising agent, the diazonium salt is reduced to N_2 and the biphenyl $(p\text{-}RC_6H_4)_2$. Cyclic voltammetry in CH_2Cl_2 confirms that the oxidation of the neutral chromium complex is a reversible one-electron process [E_p — 0.04 volts vs. saturated calomel electrode (1*M* in LiCl)]. At room temperature solutions of the cation do not exhibit an ESR signal. However, in CH_2Cl_2 at liquid nitrogen temperature, a well defined spectrum showing three-fold anisotropy of the g factor [$g_1 = 2.102$, $g_2 = 2.026$, $g_3 = 1.992$ ($g_{ave} = 2.041$)] and ^{31}P hyperfine coupling [$A_1 = 29.7G$, $A_2 = 33.6G$, $A_3 = 30.5G$, ($A_{ave} = 31.3G$)] is observed.

$(C_6Me_6)Mo(CO)_3$ also reacts with $[p\text{-}RC_6H_4N_2]^+$ to afford complexes apparently analogous to the chromium species. Although no stable products have been isolated infrared spectra of the reaction solutions in CH_2Cl_2 show initial formation of $[(C_6Me_6)Mo(CO)_2(p\text{-}RC_6H_4N_2)]^+$, the carbonyl stretching frequencies being slightly lower than those of the chromium analogues [R = H, ν(CO) 2017, 1961; ν(NN) 1673 cm^{-1}]. Prolonged reaction between $(C_6Me_6)Mo(CO)_3$ and $[p\text{-}RC_6H_4N_2]^+$ affords a second unstable dicarbonyl species in which ν(CO) again depends on the arylazo substituent [R = H, ν(CO) 2081, 2006 cm^{-1}; R = NO_2, ν(CO) 2092, 2025 cm^{-1}] but as yet these species remain uncharacterised.

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