Reactions of (Acenaphthylene)chromium Tricarbonyl with Organolithium Compounds, Trifluoroacetic Acid, and Organotin Hydrides

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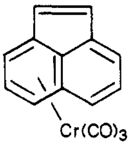
The reactivity of (acenaphthylene)chromium tricarbonyl (I) has been studied. Lithiation at the 3-position of the ligand is facile, and the resulting species was used, in situ, in further reactions with D_2O, CH_3I, $(CH_3)_3SiCl$, $BrCH_2CH_2Br$, CH_3CHO, and C_6H_5CHO to provide derivatives of I substituted in the 3-position. Reactions of I with lithium salts of four tertiary carbanions (LiR, R = $C(CH_3)_2CN$, $C(CH_3)_2CO_2C_2H_5$, $C(CH_3)_2CON(C_2H_5)_2$, and $C(CH_3)_3$) result in addition of the carbanion to the coordinated hydrocarbon; subsequent oxidation using I_2 yields monosubstituted acenaphthylenes $RC_{12}H_7$ and a coupled product, $R_2C_{24}H_{12}$. The former product occurs as a mixture in which the 3-substituted isomer is the predominant species (>90%). Crystal structure studies on 3-$C_{12}H_7C(CH_3)_2CO_2C_2H_5$ and on $C_{24}H_{12}[C(CH_3)_2CON(C_2H_5)_2]_2$ are reported. Butyllithium adds to the double bond in I, and, after protonation, one can isolate $Cr(CO)_3(\eta\text{-}1\text{-}C_4H_9C_{12}H_7)$. Free radical addition of trimethyltin hydride to this double bond is also seen, forming $Cr(CO)_3[\eta\text{-}1\text{-}(CH_3)_3SnC_{12}H_7]$. When dissolved in neat trifluoroacetic acid, I undergoes a unique oxidative coupling reaction through the hydrocarbon giving a product $Cr(CO)_3(\eta\text{-}C_{24}H_{18})$. A number of anticipated reactions of I were found not to occur.

Introduction

(Acenaphthylene)chromium tricarbonyl (I) was first reported by King and Stone[1] in 1960. This is apparently the only example of a η^6 complex of this interesting fused ring polycyclic hydrocarbon, although η^2-acenaphthylene complexes of chromium,[2] iron,[3,4] manganese,[5] and platinum[6] are also known. The bimetallic complex $Fe_2(CO)_5(\eta^5,\eta^3\text{-}C_{12}H_8)$ has also been reported.[7]



I

There are a number of reasons to be interested in the chemistry of I. One is the general interest in metal complexes of fused polycyclic hydrocarbons, evident from the rapidly expanding literature on this topic. Haptotropic rearrangement processes have been a specific focal point in current research; the migration of a metal group between fused five- and six-membered rings, mainly in complexes contain a fluorenyl ligand,[8] and between two six-membered rings in naphthalene complexes[9] receiving primary attention. Complex I is particularly interesting in this regard since either type of process could conceivably occur; indeed the significant theoretical paper[10] in this area alerts one to possible interesting results in such a study. Complex I also presents the opportunity for diverse studies on chemical reactivity. The hydrocarbon undergoes facile and reversible oxidation–reduction chemistry and the "free" double bond in the hydrocarbon is known to have considerable reactivity (toward hydrogenation and to Diels–Alder and other reactions). One expects these types of behavior to be modified upon coordination to a metal. Reactivity of arene metal complexes toward nucleophilic reagents has been much studied with results finding application in organic synthetic procedures.[11] There are only a few references to studies in the area with metal complexes of fused polycyclic aromatic hydrocarbons; however, the usefulness of this type of reaction with complexes of monocyclic arenes makes this a potentially important subject. Finally, we note the unusual color (intense purple) of I. Most chromium tricarbonyl complexes of fused aromatic hydrocarbons are red or yellow (the one notable exception being the complex of anthracene which is also purple). Interesting photochemistry of I seems a distinct possibility.

We have attempted to carry out a variety of reactions with I. While certain types of reactivity of I were unexpectedly not achieved, we were presented with success in several distinct areas: in metalation, in addition of carbanions, and in free radical additions to the double bond. Herein we describe our studies on this interesting molecular species.

Experimental Section

All manipulations were carried out under dry nitrogen or under vacuum by using a standard vacuum line. Infrared spectra were recorded on a Beckman Model 4230 spectrometer and ^1H NMR spectra were obtained with IBM WP 200 or WP 270 spectrometers, with chemical shifts (δ) measured *vs.* internal Me_4Si. UV–vis data were recorded with a Cary 118 UV–vis spectrophotometer.

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High-resolution mass spectra were obtained on a AEI MS 902 or a MS 80RF mass spectrometer. Melting points (uncorrected) were determined in sealed capillaries.

Solvents were dried before use by standard procedures. Commercially obtained reactants were used without further purification.

Synthesis of $Cr(CO)_3(\eta^6\text{-}C_{12}H_8)$ (I). The literature procedure is reported to give a 6% yield of I.[1] We were able to improve this yield substantially following the procedure given below.

A mixture of 4.18 g (18.9 mmol) of $Cr(CO)_6$ and 4.08 g (26.8 mmol) of acenaphthylene was heated (at reflux) under nitrogen in 250 mL of dimethoxyethane for 72 h. After being cooled, the solution was filtered through Celite (a commercial diatomaceous earth) and the filtrate concentrated to a few milliliters of a viscous, purple solution. The crude product was transferred to a 50 × 3.5 silica gel column and chromatographed with pentane until all of the excess yellow acenaphthylene had eluted. Diethyl ether was then used to elute the purple product. Evaporation of the eluent yields 2.8 g (51% yield) of the purple crystalline product. No further purification is required; however, the product may be recrystallized from $CHCl_3$/hexane mixtures; mp 127–129 °C; IR spectrum (CH_2Cl_2) ν(CO) 1968 (s), 1886 (s); ^1H NMR ($CDCl_3$) δ 5.33 (pseudo t, H_4), 6.09 (d, J_{45} = 6.4 Hz, H_5), 6.12 (d, J_{34} = 5.9 Hz, H_3), 7.14 (d, J_{12} = 5.2 Hz, H_2), 7.19 (d, H_1), 7.50–7.65 (m, H_6–H_8); UV–vis (in C_6H_{12}) 215 (ϵ 53 000), 287 (5200), 321 (6900), 331 (6500), 338 (6900), 525 nm (3700); UV–vis (in $(C_2H_5)_2O$) 325 (ϵ 7000), 333 (7000), 339 (7300), 523 nm (3900) (lit.[20] (in C_6H_{12}) 215 (ϵ 38 500), 349 nm (7420); the reported spectrum[1] gives only the UV absorptions). Anal. Obsd (Calcd for $C_{15}H_8CrO_3$): parent peak 287.9879 (287.9876).

Lithiation of I. Subsequent Reactions of the Lithiated Species. Lithiation of I was accomplished by using lithium diisopropylamide, LDA, which was introduced in two different ways. The first method involved the use of a weighed sample of commercial LDA. Since LDA is very air-sensitive, the handling, weighting, and storing of this material were done in a nitrogen-filled drybag. Although this material appears to dissolve only partially, this fact did not affect the outcome of the reaction. The second method involved addition of commercial *n*-butyllithium in diethyl ether to a solution of $NH(i\text{-}C_3H_7)_2$ in THF at 0 °C. A homogeneous solution of LDA was obtained after the mixture was stirred about 30 min. In reactions of the latter solutions with I, tetramethylethylenediamine, TMEDA, was usually added to be in accord with procedures described in the literature.[12] We found no evidence that one method would give better results; however, the second procedure seemed a little easier and less costly.

Preparation of $Cr(CO)_3(\eta^6\text{-}3\text{-}C_6H_5CHOHC_{12}H_7)$. A sample of I (0.199 g, 0.69 mmol) in 5 mL of THF was added to a solution containing 0.71 mmol of LDA (see procedure described above) and 0.11 mL (0.71 mmol) of TMEDA in 10 mL of THF at −42 °C. After 20 min 0.1 mL (1.0 mmol) of C_6H_5CHO in 2.0 mL of THF was added. The solution was stirred for 10 min at −42 °C and warmed rapidly to room temperature (10 min), and then four drops of CH_3CO_2H were added with stirring. The solution was filtered through Celite, and then the solvent was removed in vacuo. The residue was placed on a 30 × 2.5 silica gel chromatography column. Two purple bands eluted with 1:1 CH_2Cl_2/hexane. These bands were collected; evaporation of solvent in each left dark purple solids which were crystallized from $(C_2H_5)_2O$/pentane. The first fraction was found to be I [0.044 g (22% recovery)]; the second [0.026 g (10% yield)] was identified as the title compound: mp 140 °C dec; IR (CH_2Cl_2) 1967 (s), 1905 (m), 1877 (m) cm^{-1}; ^1H NMR δ 2.76 (s, CH), 5.91 (d, J_{45} = 6.7 Hz, H_4), 6.16 (br s, OH), 6.24 (d, H_5), 7.08 (d, J_{12} = 5.3 Hz, bridge CH), 7.14 (d, bridge CH), 7.28–7.65 (m, H_6–H_8 and phenyl protons). Anal. Obsd (Calcd for $C_{22}H_{24}CrO_4$): parent peak 394.0390 (394.0293).

Preparation of $Cr(CO)_3(\eta^6\text{-}3\text{-}CH_3CHOHC_{12}H_7)$. Solid LDA (0.18 g, 1.7 mmol) was added to a solution of 0.20 g (0.71 mmol) of I in 15 mL of THF at −42 °C. An infrared spectrum taken after 15 min contained new peaks at 1942 (m), 1837 (m), and 1811 (w) cm^{-1}. When no further change was detected in the IR after 30 min, 0.1 mL of CH_3CHO in 2.0 mL of THF was added. An IR spectrum, after 10 min, contained ν(CO) similar to those of the starting material. The solution was warmed, and five drops of CH_3CO_2H were added. Workup was carried out as described above. Starting material was not recovered; the product [0.022 g (10% yield)] was a purple crystalline solid: mp 78–80 °C; IR (CH_2Cl_2) 1969 (s), 1906 (m), 1875 (m) cm^{-1}; ^1H NMR δ 1.61 (br s, CH_3), 2.56 (br s, CH), 5.27 (br s, OH), 5.72 (d, J_{45} = 6.3 Hz, H_5), 6.23 (d, H_4), 7.22, 7.56–7.66 (m, H_1–H_2, H_6–H_8, aromatic protons). Anal. Obsd (Calcd for $C_{17}H_{12}CrO_3$): parent peak 331.9936 (332.0137).

Preparation of $Cr(CO)_3(\eta^6\text{-}3\text{-}CH_3C_{12}H_7)$. A similar procedure, using CH_3I to react with the lithiated intermediate, produced this compound in 7% yield: mp 128–131 °C; IR (CH_2Cl_2) 1966 (s), 1899 (m), 1874 (m) cm^{-1}; ^1H NMR δ 2.59 (s, CH_3), 5.20 (d, J_{45} = 6.5 Hz, H_4), 6.5 (d, H_5), 7.19 (d, J_{12} = 5.2 Hz, H_2), 7.23 (d, H_1), 7.48–7.66 (m, H_6–H_8, aromatic protons). Anal. Obsd (Calcd for $C_{16}H_{10}CrO_3$): parent peak 302.0052 (302.0032).

Preparation of $Cr(CO)_3(\eta^6\text{-}3\text{-}Me_3SiC_{12}H_7)$: prepared in a similar procedure, using $(CH_3)_3SiCl$: yield 15%; mp 122–125 °C dec; IR (CH_2Cl_2) 1968 (s), 1906 (s), 1886 (s) cm^{-1}; ^1H NMR δ 0.49 (s, Me_3Si), 5.39 (d, J_{45} = 6.4 Hz, H_4), 6.00 (d, H_5), 7.22 (s, H_1, H_2), 7.54–7.63 (m, H_6–H_8). Anal. Obsd (Calcd for $C_{18}H_{16}CrO_3Si$): parent peak 360.0274 (360.0269).

Preparation of $Cr(CO)_3(\eta^6\text{-}3\text{-}DC_{12}H_7)$. Quenching the intermediate lithio species with D_2O, and workup as described, yields this species in 7% yield. The ^1H NMR lacks the H_3 resonance at δ 6.12, and the H_4 triplet in the undeuteriated species at δ 5.33 appears here as a doublet (J_{45} = 6.5 Hz).

Preparation of $Cr(CO)_3(\eta^6\text{-}3\text{-}BrC_{12}H_7)$. Addition of $BrCH_2CH_2Br$ to the lithiated precursor, and workup as described, gave a 24% yield of this compound: mp 125–128 °C; IR (CH_2Cl_2) 1976 (s), 1912 (s) cm^{-1}; ^1H NMR δ 5.55 (d, J_{45} = 6.6 Hz, H_4), 6.05 (d, H_5), 7.21 (d, J_{12} = 5.3 Hz, H_2), 7.25 (d, H_1), 7.53–7.67 (m, H_6–H_8). Anal. Obsd (Calcd for $C_{15}H_7BrCrO_3$): parent peak 365.8985 (365.8982).

Reactions of I with Nucleophiles. Lithium Isobutyronitrile. Lithium diisopropylamide (LDA) was generated in situ by the addition of 2.8 mL (4.5 mmol) of 2.6 M $n\text{-}C_4H_9Li$ to a solution of 0.63 mL (4.5 mmol) of diisopropylamine in 15 mL of THF under nitrogen at 0 °C. The reaction was presumed to have proceeded to completion after 20 min, yielding a solution containing 4.5 mmol of LDA. This reaction time was identical with that used in similar reactions.[12] Isobutyronitrile (0.41 mL, 4.5 mmol) was added, and the mixture was stirred for 30 min at 0 °C after which 0.69 mL (4.5 mmol) of tetramethylethylenediamine (TMEDA) was added and the solution chilled to −60 °C. Upon addition of a solution of 0.437 g (1.5 mmol) of I in 10 mL of THF, a red solution was formed. After 45 min at −60 °C, a solution of 2 g of I_2 in 10 mL of THF was added from an addition funnel and the solution allowed to stir overnight while being warmed to room temperature. The solution was filtered through Celite, and solvent was evaporated from the filtrate. The residue was extracted with 35 mL of diethyl ether. The ether extract was washed twice with 10 mL of 10% aqueous $NaHSO_3$, once with 10 mL of 2 M HCl, once with 10 mL of water, twice with 10 mL of saturated $NaHCO_3$, once with 10 mL of water, and once with 10 mL of a saturated NaCl solution. The ether layer was dried with $MgSO_4$ and the ether was evaporated to yield a red oil. This was chromatographed on a 30 × 2.5 cm silica gel column with a 2:3 mixture of $CHCl_3$/hexane. Two fractions were eluted; the first gave an orange-red oil after evaporation of the solvent. This was shown to be a mixture of several isomers of the formula $C_{12}H_7C(CH_3)_2CN$ [0.175 g (53% yield)]. The primary isomer in this mixture is the isomer with the substituent group in the 3-position; ^1H NMR data were used to reach this conclusion (vide infra): ^1H NMR δ 1.94 (s, CH_3), 7.12 (d, J_{18} = 5.4 Hz, CH), 7.49–7.84 (m, 5 aromatic and one CH proton). Anal. Obsd (Calcd for $C_{16}H_{13}N$): parent peak 219.1049 (219.1045).

A second product was eluted with CH_2Cl_2 and yielded 0.0006 (0.1% yield) of $C_{24}H_{12}[C(CH_3)_2CN]_2$: a red solid; mp 221–224 °C; ^1H NMR δ 2.01 (s, CH_3), 7.58–8.14 (m, 12 aromatic ^{H}). Anal. Obsd (Calcd for $C_{32}H_{24}N_2$): parent peak 436.1941 (436.1934).

Extensive effort was directed to assessing the effect of temperature, time, and the number of moles of nucleophile on the isomer distribution in this reaction. The methyl proton region in ^1H NMR spectra generally contained several singlet resonances, the one for $3\text{-}C_{12}H_7C(CH_3)_2CN$ at δ 2.01 always being the largest.

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The other methyl resonances (δ 1.78 and 2.22) were assumed to be from other isomers; since these species were never present in large quantities and since separation was not achieved, their actual identity is unknown.

For reactions with other nucleophiles similar results were seen; one isomer predominated while traces of other isomers were also detected by ^{1}H NMR.

Lithium Ethyl Isobutyrate. Samples of 0.442 g (1.5 mmol) of I and 4.5 mmol of $Li[C(CH_3)_2CO_2C_2H_5]$ were reacted at −60 °C as described. Three products were isolated after chromatography. The first product was identified by ^{1}H NMR as acenaphthylene (0.159 g, 68% yield). The second fraction yielded 0.130 g (20% yield) of $3\text{-}C_{12}H_7[C(CH_3)_2CO_2C_2H_5]$ as a yellow solid, mp 53–56 °C. Crystals suitable for X-ray diffraction study were grown by slow evaporation of a pentane solution of the compound under nitrogen. Details of the crystallographic structure determination are reported in Table I. ^{1}H NMR δ 1.12 (t, J = 7.1 Hz, CH_3 of the ethyl group on the ester), 1.74 (s, CH_3), 4.14 (q, CH_2), 7.01 (d, J_{18} = 5.4 Hz, CH), 7.16 (d, CH), 7.44–7.80 (m, 5 aromatic protons). Anal. Obsd (Calcd for $C_{18}H_{18}O_2$): parent peak 266.1308 (266.1302).

The third fraction was eluted with CH_2Cl_2 and yielded 0.080 g (19% yield) of $C_{24}H_{12}[C(CH_3)_2CO_2C_2H_5]_2$, a red tar which would not crystallize: ^{1}H NMR δ 1.15 (t, CH_3 of the ethyl group on the ester), 1.80 (s, CH_3), 4.12 (q, CH_2), 7.09 (s, 2 ^{1}H), 7.50–8.05 (m, 10 ^{1}H). Anal. Obsd (Calcd for $C_{36}H_{34}O_4$): parent peak 530.2498 (530.248).

Lithium *N,N*-Diethylisobutyramide. Reaction of 0.453 (1.6 mmol) of I with 4.5 mmol of $Li[C(CH_3)_2CON(C_2H_5)_2]$ at −60 °C yielded 0.097 g (41% yield) of acenaphthylene and two additional products after chromatography. The first, 0.195 g (42% yield) of $3\text{-}C_{12}H_7[C(CH_3)_2CON(C_2H_5)_2]$, was isolated as a yellow solid from the second fraction: mp 68–70 °C; ^{1}H NMR δ 1.14 (t, J = 7.1 Hz, CH_3 of the amide group), 1.65 (s, CH_3), 2983 (q, CH_2), 6.49 (d, J = 5.4 Hz, CH), 7.11 (d, CH), 7.44–7.79 (m, 5 aromatic protons). Anal. Obsd (Calcd for $C_{23}H_{23}NO$): parent peak 293.1779 (293.1774).

A 16% yield (0.975 g) of $C_{24}H_{12}[C(CH_3)_2CON(C_2H_5)_2]_2$ was isolated from the third fraction (eluted with CH_2Cl_2); mp 210–219 °C dec. Crystals of this red solid suitable for X-ray diffraction were grown from $CHCl_3$/pentane. Details of the crystallographic structure determination are described in Table II. ^{1}H NMR: δ 0.48 (t, CH_3 of the amide group), 1.08 (t, CH_3 of the amide group), 1.68 (s, CH_3), 2.91 (q, CH_2), 3.38 (q, CH_2), 7.49–8.09 (m, CH and aromatic protons). Anal. Obsd (Calcd for $C_{40}H_{44}N_2O_2$): parent peak 584.3406 (584.3392).

***tert*-Butyllithium.** The reaction of 0.449 (1.6 mmol) of I and 2.6 mL (4.5 mmol) of 1.7 M $t\text{-}C_4H_9Li$ produced a red tar, $C_{12}H_7C(CH_3)_3$. A $C_{24}H_{12}R_2$ product was not obtained: ^{1}H NMR δ 1.59 (s, t-Bu), 7.05 (d, J = 5.4 Hz, CH), 7.43–7.48 (m, CH and six aromatic protons). Anal. Obsd (Calcd for $C_{16}H_{16}$): parent peak 208.1253 (208.1248).

Reactions of I with Nucleophiles and CF_3COOH. The procedure described above was used for experiments that follow with one modification. Before the addition of I_2, a fivefold excess of trifluoroacetic acid was added, and the mixture was stirred (30 min at −60 °C). The consequence of this procedure was a decrease in the amount of unsubstituted acenaphthylene, the elimination of the coupled product, and an increased yield of the substituted acenaphthylene.

$Li[C(CH_3)_2CN]$ and CF_3CO_2H. A reaction was carried out with 4.5 mmol of lithium isobutyronitrile, 4.5 mmol of TMEDA, and 0.423 g (1.5 mmol) of I; addition of 1.7 mL (22 mmol) of CF_3COOH followed by I_2 and workup as described above yielded 0.0076 g (3% yield) of acenaphthylene and 0.093 g (20% yield) of $3\text{-}C_{12}H_7[C(CH_3)_2CN]$.

$Li[C(CH_3)_2CO_2C_2H_5]$ and CF_3CO_2H. This reaction, carried out as described above, yielded 0.018 g (8% yield) of acenaphthylene and 0.192 g (47% yield) of $3\text{-}C_{12}H_7[C(CH_3)_2CO_2C_2H_5]$.

$Li[C(CH_3)_2CON(C_2H_5)_2]$ and CF_3CO_2H. This reaction yielded 0.044 g (10% yield) of $3\text{-}C_{12}H_7[C(CH_3)_2CON(C_2H_5)_2]$.

***tert*-Butyllithium and CF_3CO_2H.** This reaction yielded 0.172 g (56% yield) of $3\text{-}C_{12}H_7C(CH_3)_3$.

Reactions of Acenaphthylene with Nucleophiles. The procedure described above (without acid addition) was followed, substituting acenaphthylene for I in the procedure. The same molar ratios of reactants were employed.

Lithium Isobutyronitrile. Chromatography of the products of this reaction yielded three fractions. The first was a mixture of acenaphthylene (6.3% yield) and acenaphthene (5.0% yield). The second fraction yielded a yellow oil containing $C_{12}H_7[C(CH_3)_2CN]$ (3% yield) and an acenaphthene product, $C_{12}H_9[C(CH_3)_2CN]$ (10% yield). Identification of these products was made by ^{1}H NMR and mass spectroscopy. A third fraction, red in color, was eluted with CH_2Cl_2 and contained a complex mixture of products (oligomers of acenaphthene) that could not be separated or characterized.

Lithium Ethyl Isobutyrate. Lithium *N,N*-Diethylisobutyramide. Following the procedures described above these reactions resulted in recovery of 100% of unreacted starting material, $C_{12}H_8$.

***tert*-Butyllithium.** A red oil was obtained as the only product; spectroscopic data showed that this was a mixture of oligomers similar to that obtained in the reaction of $C_{12}H_8$ and $Li[C(CH_3)_2CN]$.

Reaction of I with $LiBH_4$. Samples (0.014 g, 0.05 mmol) of I and 0.001 g (0.05 mmol) of $LiBH_4$ were sealed in an NMR tube as a solution of THF-d_8. ^{1}H NMR spectra were recorded periodically over a 10-day period. Only the reaction of I to form $C_{12}H_8$ and $(THF\text{-}d_8)_nCr(CO)_{6-n}$ (n = 2, 3) was observed.

Reaction of I with *n*-Butyllithium Followed by H_2O Addition. A 0.287-g (1.0-mmol) sample of I was dissolved in 15 mL of THF at −78 °C; then 0.8 mL (2.1 mmol) of 2.6 M $n\text{-}C_4H_9Li$ was added over a 40-min period with stirring. The color of the reaction mixture turned red. After the mixture was allowed to warm to room temperature, a small excess of water was added. The solution was stirred for 30 min and then filtered through Celite. Solvent was evaporated from the filtrate to yield an orange oil. The oil was dissolved in a small volume of 1:1 CH_2Cl_2/hexane and chromatographed on a 30 × 2.5 cm silica gel column. A mixture of 1:1 CH_2Cl_2/hexane was used to elute an orange band. Evaporation of the eluent followed by crystallization of the residue from CH_3/hexane yielded 0.031 g (9% yield) of orange-brown solid, $Cr(CO)_3(\eta\text{-}C_{12}H_7C_4H_9)$: mp 105–107 °C; IR 1952 (s), 1878 (s) cm^{-1}; ^{1}H NMR δ 0.79–0.93 (m), 1.11–1.52 (m), 1.68–1.80 (m, 9 ^{1}H), 3.39–3.51 (m, 3 ^{1}H), 5.11 (d, J = 6.2 Hz, 1 ^{1}H), 5.29 (t, J = 6.2 Hz, 1 ^{1}H), 5.59 (d, ^{1}H), 5.95 (d of d, J = 9.9, J = 3.7 Hz, 1 ^{1}H), 6.08 (d of d, J = 2.1, J = 4.3 Hz, 1 ^{1}H), 6.26 (d of d, J = 2.1, J = 9.9 Hz, 1 ^{1}H). Anal. Obsd (Calcd for $C_{19}H_{18}CrO_3$): parent peak 346.0621 (346.0656).

If H_2O in this reaction is replaced by D_2O, a similar product was obtained with an appropriate mass spectrometric peak match ($P + 1^+$). In the ^{1}H NMR of this deuteriated product, the multiplet at δ 3.39–3.51 had a relative intensity of 2.

Reaction of I with Trimethyltin Hydride. A mixture of I (0.139 g, 0.48 mmol), azobis(isobutyronitrile), AIBN (0.00759 g, 0.05 mmol), and trimethyltin hydride (1.0 mL, 7 mmol) in 10 mL of benzene was prepared in a reaction tube that was sealed under vacuum. The tube was heated at 70 °C for 7 h and then allowed to cool slowly overnight. The tube was then opened, and the dark red solution was filtered through Celite and the filtrate evaporated to a crude red oil. The oil was transferred to a 30 × 2.5 cm silica gel/hexane column with a minimum of a 1:1 mixture of CH_2Cl_2/hexane and chromatographed with 50 mL of hexane. A 1:1 mixture of CH_2Cl_2/hexane was used to elute a single red fraction. Evaporation of the eluent yielded another red oil; when the mixture was dissolved in hexane and chilled to −20 °C, 0.027 g (12% yield) of orange solid $Cr(CO)_3[(\eta\text{-}C_{12}H_9Sn(CH_3)_3]$ precipitated: mp 98–101 °C dec; IR (CH_2Cl_2) 1959 (s), 1885 (s) cm^{-1}; ^{1}H NMR δ 0.13 (s, CH_3), 3.2–3.5 (m, H_1, $H_{2'}$), 3.84 (d of d, J_{12} = 9.8, $J_{22'}$ = 18.7 Hz, H_2), 5.51 (d, J = 3.8 Hz, 2 ^{1}H, H_5, H_3), 5.88 (pseudo t, J = 3.8 Hz, H_4), 6.88 (d, J = 8.9 Hz, H_8), 7.14–7.38 (m, H_6, H_7). Anal. Obsd (Calcd for $C_{18}H_{18}CrO_3$): parent peak 451.9680 (451.9677).

Reaction of I with Organotin Hydrides. A similar procedure using tri-n-butyltin hydride gave a red oil that refused to crystallize. Its ^{1}H NMR spectrum contained resonances appropriate to the expected product, but the mass spectrum did not give a parent peak match. (The highest m/e peak was 580, vs. 578 (calculated for this product.) The reaction of I with triphenyltin hydride resulted in an orange solid being isolated, along with some hexaphenyldistannane. The ^{1}H NMR of the orange solid had

Table I. Summary of Crystal Data and Intensity Collection[a] for IIIb

empirical formula	$C_{18}H_{18}O_2$
fw	266.3
cryst dimens	0.08 × 0.35 × 0.40
temp, K	293
cell parameters	
a, Å	24.372 (5)
b, Å	8.084 (2)
c, Å	15.101 (4)
β, deg	15.101 (4)
space group	P_{bcn}
Z	8
d(calcd), g/cm^3	1.19
abs coeff, μ, cm^{-1}	0.71
Nicolet diffractometer[b]	P3/F
scan type	ω
scan range	
deg below 2θ (Kα_1)	
deg above 2θ(Kα_2)	
scan speed, deg/min	3.45–29.3
bkg/scan ratio	1.0
2θ limits, deg	3.5–45
$(\sin\theta)/\lambda_{max}$	0.538
unique data, theoretical	1950
$F_0 > 3\sigma(F_0)$	1013
p; weight = $[\sigma^2(F) + p^2F^2]^{-1}$	0.03
discrepancy indices	
R_1	0.0689
R_2	0.0690
goodness of fit	1.30
observn/variable ratio	5.33

[a] Method similar to: Haller, K. J.; Enemark, J. H. *Inorg. Chem.* **1978**, *17*, 3552. Scattering factor tables from *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV. [b] Diffractometer equipped with a graphite-monochromated molybdenum Mo Kα radiation source. [c] Symmetric scan, 1.25° wide.

resonances appropriate to the expected 1:1 adduct.

Reaction of I with CF_3CO_2H. A 0.649-g (2.3-mmol) sample of I was placed in a reaction tube and 5 mL of CF_3CO_2H distilled into this vessel under vacuum; the vessel was then sealed and allowed to stand for 2.5 h at 20 °C. The purple color of I was rapidly replaced by a bright orange color in a process accompanied by the evolution of gas and precipitation of an orange solid. The acid was distilled from the reaction tube under vacuum and the orange-brown residue extracted with benzene. The volume of the orange benzene extract was reduced and the resulting dark red solution filtered through glass wool. Hexane was added and the mixture chilled to precipitate 0.269 g (54% yield) of an orange solid with composition $C_{24}H_{18}Cr(CO)_3$. The benzene-insoluble materials in the reaction tube were green in color and presumably are Cr(III) species derived from decomposition. Repetition of the reaction in the absence of light gave the same results. Repetition of the reaction using benzene/CF_3COOH mixtures with a high acid concentration led to the same observed color changes, but isolation of a pure product was unsuccessful. Stoichiometric reaction of the reactants led to the observation of no reaction (in benzene): mp 165–166 °C dec; IR (CH_2Cl_2) 1959 (s), 1882 (s) cm^{-1}; ^{1}H NMR (C_6D_6) δ 3.12 (d, $J_{22'}$ = 18 Hz, H_2), 3.95 (d of d, $J_{12'}$ = 9.0 Hz, $H_{2'}$), 4.70 (d of d, J_{34} = 5.4, J_{45} = 6.4 Hz, H_4), 4.86 (d, H_5), 5.22 (d, H_3), 5.58 (d of d, J_{12} = 1.9 Hz, H_1), 6.6–7.05 (m, 3 ^{1}H, H_6–H_8). Anal. Obsd (Calcd for $C_{27}H_{18}CrO_3$): parent peak 442.0661 (442.0656).

If CF_3COOD is used in place of CF_3COOH, the doublet of doublet of resonances at 3.95 ppm collapses to a doublet with $J_{12'}$ = 9 Hz, indicating deuterium incorporation at carbon 2. Concurrently, the signal at δ 3.12 disappears.

A rather extensive series of other reactions of I were unsuccessful. This includes reactions at the "free" double bond in I including oxymercuration, attempted photodimerization, 4 + 2 cycloaddition with C_5Cl_6, a 1,3 dipolar addition with 9-diazofluorene, and attempts to complex the double-bond transition metals (reactions with $IrCl(CO)[P(C_6H_5)_3]_2$, $Fe(CO)_5$, $Mn(CO)_2(THF)(\eta\text{-}C_5H_5)$); all of these reactions resulted in decomposition with no notable organometallic products. In each of these cases the free ligand is known to react. Attempts to reduce I using Na/Hg also resulted in decomposition.

Table II. Summary of Crystal Data and Intensity Collection[a] for IVc

empirical formula	$C_{40}H_{44}N_2O_2$
fw	584.8
cryst dimens	0.06 × 0.09 × 0.27
temp, K	293
cell parameters	
a, Å	10.760 (5)
b, Å	8.683 (4)
c, Å	17.692 (9)
β, deg	105.62 (4)
space group	$P2_1/n$
Z	2
d(calcd), g/cm^3	1.22
abs coeff, μ, cm^{-1}	0.69
Nicolet diffractometer[b]	P3/F
scan type	θ–2θ
scan range	
deg below 2θ(Kα_1)	1.0
deg above 2θ(Kα_2)	1.0
scan speed, deg/min	2–29.3
bkgd/scan ratio	c
2θ limits, deg	4–42.93
$(\sin\theta)/\lambda_{max}$	0.515
unique data, theoretical	1820
$F_0 > 3\sigma(F_0)$	985
p; weight = $[\sigma^2(F) + p^2F^2]^{-1}$	0.04
discrepancy indices	
R_1	0.0926
R_2	0.0930
goodness of fit	1.34
observn/variable ratio	4.65

[a] Method similar to: Haller, K. J.; Enemark, J. H. *Inorg. Chem.* **1978**, *17*, 3552. Scattering factor tables from: *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV. [b] Diffractometer equipped with a graphite-monochromated molybdenum Mo Kα radiation source. [c] Backgrounds obtained by profile analysis.

Crystal Structures. A summary of the crystal structure data for IIIb and IVc is provided in Tables I and II, respectively. Thermal parameters, bond lengths and bond angles for both compounds are found in the supplementary material.

Discussion

(Acenaphthylene)chromium tricarbonyl (I) was prepared in ~50% yield by the reaction of $Cr(CO)_6$ and this hydrocarbon. Use of a dilute solution of these reactants, a

$$Cr(CO)_6 + C_{12}H_8 \rightarrow \underset{\text{I}}{Cr(CO)_3(\eta\text{-}C_{12}H_8)} + 3CO$$

low boiling solvent, and much lengthened reaction times provided an improved yield relative to the results described in the literature.[1] We have found that adjusting reaction conditions in this way will generally improve yields in reactions of fused polycyclic aromatic ligands with $Cr(CO)_6$.[13] (Acenaphthylene)chromium tricarbonyl is a crystalline solid whose solutions have an intense purple color resulting from the absorption of 525-nm light (ϵ 3700). This absorption is assumed to be a metal–hydrocarbon charge-transfer band. In addition, I has absorptions at 338, 331, 321, and 287 nm. There are similar absorptions in the uncomplexed hydrocarbon at 340, 335, 323, 311, and 276 nm,[14] suggesting that these absorptions in I involve intraligand transitions. Compound I has carbonyl absorptions in the infrared spectrum at 1968 (s) and 1886 (s) cm^{-1}, similar to values for other chromium tricarbonyl complexes of fused ring aromatic hydrocarbons. The ^{1}H NMR spectrum contains a multiplet pattern around δ 7.6 for the three hydrogens on the uncomplexed six-membered

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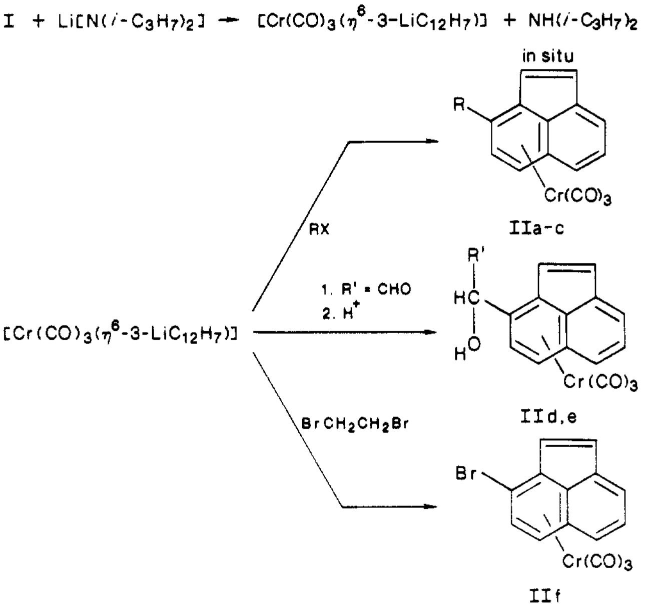
(13) Kirss, R. U., unpublished results.

(14) Linsey, A. J. *Anal. Chim. Acta* **1959**, *20*, 175.

Scheme I



ring (H_6, H_7, H_8) and two closely spaced doublets, δ 7.19 and 7.14, for the hydrogens on the double bond. Three resonances for hydrogens of the coordinated ring are shifted upfield to δ 5.33 (t, H_4), 6.09 (d, H_5) and 6.12 (d, H_3); upfield shifts are characteristic of protons on a coordinated hydrocarbon.

Assignments of ^{1}H NMR resonances to H_3, H_4, and H_5 as given above merit further comment since these assignments are important to the subsequent discussion. The higher field position and the multiplicity of the δ 5.33 resonance clearly identify this with H_4. The two doublets at δ 6.09 (J = 6.5 Hz) and δ 6.12 (J = 5.9 Hz) must therefore be from H_3 and H_5. On the surface, it seems unlikely that one could distinguish which is associated with H_3 and H_5. However, when ^{1}H NMR data on a large number of (1-substituted naphthalene)chromium tricarbonyls are assembled,[13] it can be seen that in all cases J_{23} is less than J_{34}. Translated to this system, this means that the δ 6.12 resonance should be assigned to H_3 and the δ 6.09 resonance to H_5.

The most generally successful aspect among the studies on reactivity of I involved lithiation at the hydrocarbon ring. The lithiated species was then used in a series of subsequent reactions (with D_2O, CH_3I, $(CH_3)_3SiCl$, $BrCH_2CH_2Br$, C_6H_5CHO, and CH_3CHO) to provide derivatives of I. The reaction sequence is shown in Scheme I.

Generally, the overall yields in these reactions are fairly low (10–20%); however, no effort was made to maximize yields. Our studies on the lithiation of chromium tricarbonyl complexes with fused polycyclic aromatic hydrocarbons[9,13] suggest that these lithiated species have low stabilities with respect to dissociation of the hydrocarbon, and this is probably the cause of the low yields in the reactions reported here.

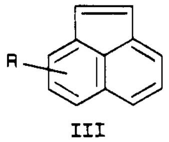
A single isomeric species is formed in these reaction sequences with the substituent group most likely at the 3-position in the hydrocarbon ring. This structural assignment relies on a number of pieces of evidence including the assignment on the ^{1}H NMR of I, discussed above. In $Cr(CO)_3(\eta^6\text{-}C_{12}H_7D)$ the doublet at δ 6.12 is lacking while the δ 6.09 resonance with a 5.9-Hz coupling is retained. It may also be pointed out that lithiations of several other metal complexes with fused polycyclic aromatic hydrocarbon ligands (metal complexes of 2,6- and 2,7-dimethoxynaphthalene, 5-methoxynaphthalene, phenanthracene) occur at analogous positions. The kinetically preferred site of lithiation of (naphthalene)chromium tricarbonyl is the 2-position, although the thermodynamically preferred site is position 1.[15]

Nucleophilic additions to I also occur primarily at position 3; MO theory justifies this result in that the p_z orbital of carbon 3 contributes substantially to the LUMO in this complex (vide infra).

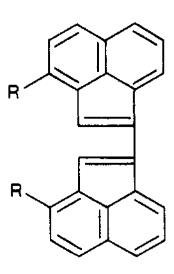
Additional study on the reactivity of I was directed to reactions with carbanionic nucleophiles. Analogous reactions with monocyclic (arene)chromium tricarbonyls have received serious attention in the last decade,[11] and in recent years this type of reaction has been used in various organic synthesis projects. The mechanism of this type of reaction is believed to involve addition of the nucleophile to the coordinated ring, producing a (η^5-cyclohexadienyl)chromium carbonyl anion that has been isolated on occasion. If the carbon to which the nucleophile has added contains a good leaving group, then its elimination produces a new organometallic species. If not, the most common procedure is to degrade this adduct using an oxidizing agent to give the substituted arene.

There are, however, only a few prior references describing reactions of metal complexes of fused polycyclic aromatic hydrocarbons with carbon nucleophiles. Semmelhack et al.[11,17] described the reaction between (naphthalene)chromium tricarbonyl and $Li[C(CH_3)_2CN]$ in THF; oxidative degradation produces $1\text{-}C_{10}H_7C(CH_3)_2CN$ along with a trace of the 2-substituted hydrocarbon. Further study was accorded to similar reactions of $Cr(L)_3(\eta\text{-}C_{10}H_8)$ (L = CO, PR_3, $PF(OCH_3)_2$), $P(OCH_3)_3$, $P(CH_3)_3$) and of $Cr(CO)_3(\eta\text{-}5\text{-}C_{10}H_7OCH_3)$ and $Cr(CO)_3(\eta\text{-}5,8\text{-}C_{10}H_6(OCH_3)_2)$ by Kundig et al.;[16-18] emphasis in these studies was directed to the regiochemistry of addition.

Reactions between I and a series of carbanion nucleophiles (LiR, R = $C(CH_3)_2CN$, $C(CH_3)_2CO_2C_2H_5$, $C(CH_3)_2CON(C_2H_5)_2$, $C(CH_3)_3$) were carried out, following closely the procedures used by other workers in this field.[11] A THF solution of the alkyllithium containing TMEDA was prepared at −60 °C and I added, the color of the solution changing immediately to red or black. After ~45 min excess iodine was added to the mixture. As an alternative, addition of CF_3CO_2H preceded addition of iodine. A workup that involved chromatography was used to separate acenaphthylene and two hydrocarbon products, III and IV. The two product species were then identified by a combination of mass spectrometry and ^{1}H NMR spectrometry and by single-crystal X-ray diffraction methods.



III



IV

The yields of IIIa–d varied but were generally in the

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[15] Treichel, P. M.; Kirss, R. U. Organometallics, following paper in this issue.

[16] Kundig, E. P.; Desobry, V. Helv. Chim. Acta 1981, 64, 1288.

[17] Kundig, E. P.; Desobry, V.; Simmons, D. P. J. Am. Chem. Soc. 1983, 105, 6962.

[18] Kundig, E. P.; Simmons, D. P. J. Chem. Soc., Chem. Commun. 1983, 1320.

Table III. Effect of Reaction Conditions on Product Distribution of the Reaction of $Cr(CO)_3(\eta\text{-}C_{12}H_8)$ with $Li[C(CH_3)_2CN]$

n^a	reaction time	reaction temp, °C	% $C_{12}H_8$	% 3-$C_{12}H_7R$	% other isomers^b
2	45 min	−60	7	30	7
2	45 min	−42	2	32	4
2	45 min	−23	29	26	0
2	45 min	0	24	37	1
1	45 min	−60	48	8	6
8	45 min	−60	0	35	6
2	24 h	0	12	36	1
2	48 h	0	31	30	0

[a] Signifies the number of equivalents of $Li[C(CH_3)_2CN]$ used per equivalent of $Cr(CO)_3(\eta\text{-}C_{12}H_8)$. [b] These yields do not include the $C_{24}H_{12}R_2$ products.

Table IV. IR Spectral Data for Intermediates in Reactions of I with Carbanions

compd	ν(CO), cm^{-1} (THF)
$C_{12}H_8Cr(CO)_3$ + RLi	1965, 1905, 1889
R = $C(CH_3)_2CN$	1965, 1905, 1899, 1815, 1795, 1728
R = $C(CH_3)_2CO_2C_2H_5$	1965, 1896, 1835, 1731
R = $C(CH_3)_2CON(C_2H_5)_2$	1960, 1896, 1790, 1730, 1716
R = $C(CH_3)_3$	1960, 1901, 1886, 1808, 1719
η^5-bis((phenylthio)methyl)-(benzene)$Cr(CO)_3^-$	1901, 1802, 1712[19]
(η^5-cyclohexadienyl-naphthalene)$Cr(CO)_3^-$	1895, 1800, 1745[20]

20–40% range, while the coupled products IVa–c (IVd was not found as a product) were typically obtained in less than 20% yield. Acenaphthylene was the remaining product. The procedure involving addition of acid generally resulted in lower amounts of acenaphthylene and eliminated IVa–c from the product mixture. Reactions of the organolithium reagents with the free hydrocarbon generally gave different results; one finds reduced species (acenaphthene) and oligomers of acenapthylene as the primary products of these reactions. These results indicate that the coordinated metal must be influential in these processes.

Reactions attempted using a number of other carbanions were not successful. This includes stabilized primary and secondary carbanions (CH_2CN^-, $CH_2NO_2^-$, $CH_2C_6H_5^-$, $CH(CH_3)CN^-$, $CH(CH_3)CO_2C_2H_5^-$, $CH(C_6H_5)_2^-$, $\overline{CHSCH_2CH_2CH_2S}^-$) and a few tertiary carbanions ($C(C_6H_5)_3^-$, $C(CH_3)_2CONH_2^-$, and $C(CH_3)(C_6H_5)CN^-$). Thus the applicability of this type of reaction in the future appears to be severely restricted.

The proposed mechanism for the nucleophilic aromatic substitution reaction of I involves exo attack by the nucleophile at the complexed ring to form a cyclohexadienylmetal intermediate. Upon oxidation, 1 equiv of hydride is lost to generate the substituted acenaphthylene. Evidence for a cyclohexadienyl intermediate is available from IR spectra recorded during the reaction. In all of the successful nucleophilic substitution reactions of I, new, lower energy CO stretching frequencies were observed in the infrared spectrum of the reaction mixture; these are summarized in Table IV. In each case the ν(CO) absorptions indicate that a significant amount of starting material is also present. In reactions of I with nucleophiles that did not add to the $C_{12}H_8$ ligand, no changes were observed in the CO region of the infrared spectrum. Similar infrared data have been reported in the literature for substituted (η^5-cyclohexadienyl)$Cr(CO)_3^-$ species[19] and for the (η^5-cyclohexadienylnaphthalene)$Cr(CO)_3^-$ compound.[20]

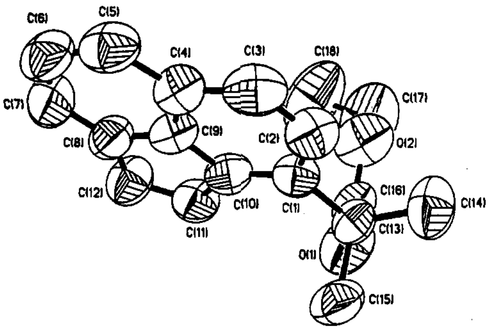

Figure 1. Structure of 3-$C_{12}H_7C(CH_3)_2CO_2C_2H_5$.

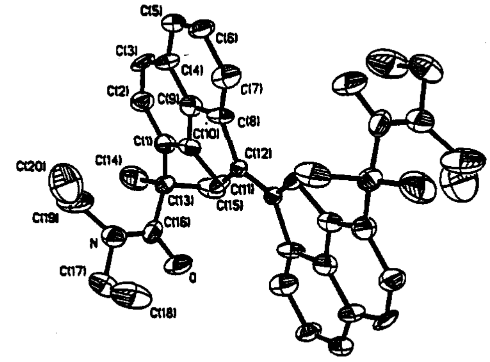

Figure 2. Crystal structure of $C_{24}H_{12}[C(CH_3)_2CON(C_2H_5)_2]_2$.

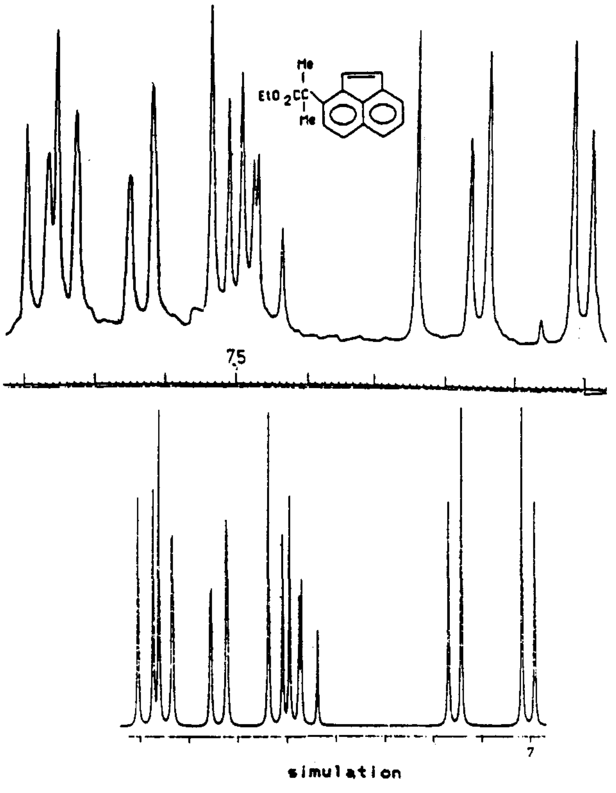

Figure 3. Aromatic region of the ^{1}H NMR spectrum of 3-$C_{12}H_7C(CH_3)_2CO_2C_2H_5$.

The products III appear to be formed as mixtures consisting of one major isomer and several minor isomers (see Table III); this conclusion is based on several methyl resonances being observed in the ^{1}H NMR spectrum of the crude mixture. In cases where the product is an oil, the isomers were not separated. However, in the one instance in which the product was a solid (compound IIIc), the

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(19) Semmelhack, M. F.; Clark, G. R.; Garcia, G. L.; Harrison, J. J.; Thebarononth, Y.; Wulff, W.; Yamashita, A. *Tetrahedron* **1981**, *37*, 3957.

(20) Rieke, R. D.; Henry, W. P. *J. Am. Chem. Soc.* **1983**, *105*, 6314.

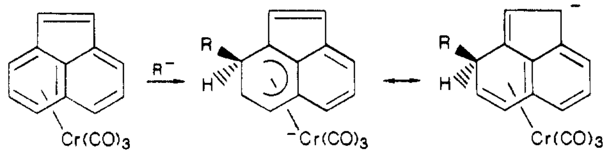
primary isomer was obtained pure after one crystallization.

A single-crystal X-ray diffraction study on IIIb gave unequivocal proof that nucleophilic attack was at the 3-position of the coordinated acenaphthylene (Figure 1). ^1H NMR had previously narrowed the choice to a structure with the substituent group on either C(3) or C(5). In addition to the methyl and methylene proton resonances, the ^1H NMR spectrum (Figure 3) contains 16 well-resolved resonances in the aromatic region (Figure 2). The pair of doublets (J = 5.4 Hz, an AB pattern centered at δ 7.09) at highest field can be assigned to the protons H_1 and H_2; in $C_{12}H_8$ these protons occur as a singlet at δ 7.09. In the unsubstituted ring, H_7 is expected to appear as a doublet of doublets, and the quartet resonance at δ 7.48 (J = 6.8, 7.9 Hz) is attributed to this proton. The coupling constants further identify the doublet resonances at δ 7.62 (J = 6.8 Hz) as due to H_8 and at δ 7.75 (J = 7.9 Hz) to H_6 noting that in the spectrum of $C_{12}H_8$ H_6 is found at lower field than H_8. The remaining resonances are doublets at δ 7.52 (J = 8.5 Hz) and δ 7.76 (J = 8.5 Hz). A doublet pattern requires these protons to reside on adjacent carbon atoms, either on H_4 and H_5 (substituent on position 3), as is known to occur, or on H_3 and H_4 (substituent on position 5). The assignment of these resonances to H_4 and H_5 can be made from the magnitude of the coupling constant (J = 8.5 Hz), so H_4 is assigned at the lower field position δ 7.76 (vide supra, H_7).

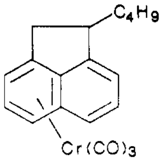
^1H NMR spectra of compounds IIIa,c,d were more difficult to analyze but generally provided similar information. In these cases the presence of minor isomers in the product complicates the analysis of the aromatic region of the spectrum.

A second hydrocarbon product was obtained in three of the four reported reactions. These species occur as red oils or solids and have the general stoichiometry $C_{24}H_{12}R_2$. The ^1H NMR spectra confirm that these are products formed by coupling two substituted acenaphthylenyl units, but the complexity of the spectra limits the amount of additional structural information that can be obtained. Thus a single-crystal X-ray diffraction study was also carried out on one of these compounds (IVc), the structure given in Figure 2 being found.

This structure is most interesting in that it provides a clue to the mechanism by which this species is formed (see Figure 2). The key point is that metal coordination on the ring receiving the nucleophilic carbon substituent is expected to be stabilized by interaction with the π orbital on C(2) which in turn directs the next step (a coupling reaction by radical or anionic attack) to C(1), viz.



Interestingly, the reaction between I and n-butyllithium gave a quite different result. When these reactants are mixed at low temperature, a color change occurred. Protonation (without I_2 degradation) yielded an organometallic product, which was identified by IR, ^1H NMR, and mass spectrometry as V, a product of addition of Bu^- and H^+ across the double bond. Significant NMR evidence includes the multiplet resonances at δ 3.15, characteristic of the saturated hydrocarbon side chain. No evidence is available on either the regiochemistry or the stereochemistry of this addition.

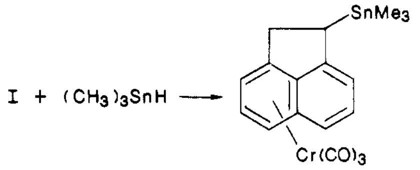


V

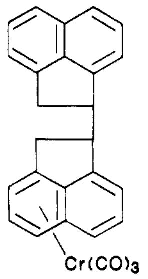
As noted above, the observed reactions of I are limited to a relatively small number of nucleophilic reagents. Reactions of a considerable number of other nucleophiles were attempted without success, solution IR data on these reaction mixtures indicating no intermediate cyclohexadienyl complex forming. One possible explanation for this pattern of reactivity comes from simple MO theory. The reactivity of an (arene)Cr(CO)$_3$ compound with a carbanion can be thought to proceed by interaction of the highest occupied molecular orbital (HOMO) of the carbanion with the lowest unoccupied molecular orbital (LUMO) of the (arene)Cr(CO)$_3$.[21] The HOMO of the carbanion should lie at lower energy than the LUMO of the chromium compound. It is possible that the HOMO energies of the primary and secondary carbanions studied are sufficiently low in energy relative to the LUMO of I that no reaction can occur. This would be in accord with the trend of LUMO energies for the anions derived from CH_3CN, CH_3CH_2CN, and $(CH_3)_2CHCN$. The electron-donating characteristics of each additional methyl group should destabilize the anion and raise the energy of its HOMO.

Attack of the nucleophile at the several positions in I can also be rationalized by MO theory. The LUMO in I is primarily a ligand orbital with p_z orbitals on C(1), C(2), C(3), and C(5) being major contributors. Attack of nucleophilic reagents at C(3) and C(1) has been substantiated in this work, and the presence of more than two isomers in these systems suggests the possibility of reaction at other sites.

Two other reactions of I were studied which involve the free double bond in this compound. It is possible to add trimethyltin hydride to I by using a free radical catalyst.



Spectroscopic data on the product do not allow identification of the regio- and stereochemistry of this species. The second reaction occurs when I is dissolved in neat CF_3CO_2H. Upon mixing a rapid color change to red occurs; workup gave a red crystalline compound with the formula $Cr(CO)_3(\eta^6\text{-}C_{24}H_{18})$ (VI). Although it is possible to identify the hydrocarbon ligand as a biacenaphthene, the precise stereochemistry of this product is also not known. Interestingly, this product is obtained only by using CF_3C-



VI

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Organometallics **1987**, *6*, 249-254

O_2H as a solvent; in dilute solution, this acid and I do not react. A possible mechanism of formation involves proton addition to carbon 1 of the free double bond followed by addition of the metal-stabilized carbonium ion another molecule of I. Oxidation by another proton (and its incorporation into the molecule) could occur with concurrent loss of Cr^{2+}, leaving the product with a biacenaphthene ligand and one metal.

Acknowledgment. We are pleased to acknowledge partial support for this work from the National Science Foundation through Grant CHE 8210497.

Supplementary Material Available: Tables of atomic coordinates and isotropic thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, and H-atom coordinates and isotropic thermal parameters for IIIb and IVc (10 pages). Ordering information is given on any current masthead page.

Metalation of the Fused Polycyclic Aromatic Ligand in (Arene)chromium Tricarbonyl Complexes: Kinetic and Thermodynamic Site Preferences

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Lithiation of the hydrocarbon ligand in chromium tricarbonyl complexes of naphthalene, 5-methoxynaphthalene, 2,6- and 2,7-dimethoxynaphthalene, and phenanthene is accomplished by reactions of these complexes with lithium diisopropylamide. The lithiated complexes decompose rapidly even at the low temperature of formation (−78 to −95 °C) but can be intercepted in reactions with various species including D_2O, CH_3I, $(CH_3)_3SiCl$, CH_3CHO, or C_6H_5CHO to give substituted derivatives of the starting material. Data are presented which indicate that for $Cr(CO)_3(\eta^6\text{-}C_{10}H_8)$ there is a kinetic preference to lithiation at C(2) and a thermodynamic preference for lithiation at C(1) of the naphthalene ligand. This permits one to optimize the synthesis of either (1-methylnaphthalene)- or (2-methylnaphthalene)chromium tricarbonyl in this reaction sequence.

Introduction

(Arene)chromium tricarbonyl complexes are known to undergo metal–hydrogen exchange (metalation) when treated with certain alkyllithium compounds.[1] It is also possible prepare (lithiobenzene)chromium tricarbonyl in a transmetalation reaction from $Cr(CO)_3(\eta\text{-}C_6H_5HgC_6H_5)$ and *n*-butyllithium.[2] This type of lithiated species has found significant recent application in organometallic and organic syntheses.[3] Complexation of an arene to chromium enhances the reactivity of the aryl protons relative to both the free arene and to other protons in the molecule (in arene substitutent groups, for example). Metalation in these organometallic systems takes place under very mild conditions, and one can exert significant control on the regiospecificity of the reaction.

Until quite recently arene metalation reactions were known only for chromium carbonyl derivatives of benzene or substituted benzenes.[4] Metalation of complexes with fused polycyclic aromatic was conspicuously absent. However, this situation was altered with the appearance of a brief report on the metalation of the naphthalene ligand in $Cr(CO)_3(\eta^6\text{-}C_{10}H_8)$ in 1984.[5] Recently we described lithiation of (2,7-dimethoxynaphthalene)- and (2,6-dimethoxynaphthalene)chromium tricarbonyl, giving a lithiated complex in situ which could then be deuteriated. Regiospecific deuterium incorporation into the ring coordinated to chromium provided labeled complexes that were further used in a study on haptotropic migrations.[6] In the course of that work it seemed reasonable to assume that the metalation of complexes of fused polycyclic aromatic hydrocarbons should be a general phenomenon.[7] Furthermore, when details of these processes were established, the further utility of these lithiated species in organic and organic synthetic projects appears to be a reasonable option.

This paper describes our studies on the metalation reactions of several chromium tricarbonyl complexes with fused polycyclic aromatic hydrocarbon ligands. An unanticipated result emerged in this study when it was observed that the position of lithiation in certain complexes was influenced by reaction conditions. Some effort was then directed to the examination of this phenomenon that is the result of a balance between kinetic vs. thermodynamic control. We will also report studies on several reactions of the lithiated species in this paper.

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