# 117. A $^{13}C$-NMR. Study of Naphthalene Chromium Complexes[1]). Correlation with Reactivity: Nucleophilic Aromatic Substitution Reactions

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## Summary

The $^{13}C$-NMR. spectra of the series of complexes $\eta^6$-naphthalene · $CrL_3$ (L=CO (**1**), $PF_3$ (**2**), $PF_2OMe$ (**6**), $P(OMe)_3$ (**3**), $C_{10}H_8$ (=3 L) (**4**) and $PMe_3$ (**5**)) are reported. Definite assignments of the $^{13}C$-NMR. resonances were made through the synthesis of $[2,3,6,7\text{-}^2H_4]$-naphthalene complexes. The coordinated ring $^{13}C$-resonances are found to undergo a smooth transition to higher field with increasing donor character of the coligands L. A correlation of the coordination shifts with the reactivity of the coordinated naphthalene is proposed. In complexes containing strong acceptor ligands the naphthalene is activated to attack by nucleophiles. Sequential treatment of complexes **1**-**4**, **6** and $[C_{10}H_8FeC_5H_5]^+[PF_6]^-$ (**7**) with stabilized carbanions and $I_2$ or Ce(IV)-salt yields $\alpha$-substituted naphthalenes in the case of **1**, **2**, **6** and **7** but not in the case of **3** and **4**. Treatment of **3** with an excess of $HBF_4$ results not in the expected metal protonation but in a novel ligand transformation to yield **6**.

**Introduction.** - When an arene is coordinated to $Cr(CO)_3$, profound changes in its reactivity occur [2] [3]: ring and benzylic H-atoms exhibit enhanced acidity, and typical arene reactions such as electrophilic aromatic substitutions are quenched. In contrast to this, the ring C-atoms are activated toward attack by nucleophiles [2]. These changes in reactivity are manifestations of the forceful electron withdrawing nature of the $Cr(CO)_3$ component, and of the ability of this group to stabilize charged intermediates. The *Umpolung* of the arene in these complexes, combined with their stability and straightforward synthesis make them increasingly attractive for organic synthesis.

Arene reactivity in metal complexes is affected by the nature of the metal and the electron density on the metal. Even within an oxidation state the latter can vary substantially depending on the donor/acceptor properties of the coligands. It has been demonstrated that the activating influence brought about by the $Cr(CO)_3$ group is modified by the replacement of even one carbonyl group by another ligand. Alkylation at the benzylic position of alkyl arenes coordinated to

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[1]) Naphthalene Complexes, Part 2. Part 1: [1].

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$Cr(CO)_2P(OPh)_3$ affords the monoalkylated product whereas the $Cr(CO)_2CS$ activated arene yields the dialkylated product selectively [4]. Apart from this elegant study, there is a scarcity of information on the effects of the coligands on the arene reactivity. In the past this was due to the absence of a synthetic method that would allow the preparation of a suitable range of arene complexes. With the synthesis of a series of new naphthalene complexes by ligand displacement from the labile bis(naphthalene)chromium [1], this is no longer the case.

We have initiated a systematic investigation of the effect of the coligands on the Cr-naphthalene bond and on the reactivity of the coordinated arene. In this paper we report the synthesis of a new naphthalene complex, present an analysis of the $^{13}$C-NMR. spectra of coordinated naphthalene, and study the reactivity of naphthalene complexes with C-nucleophiles.

**Results and Discussion.** - *Synthesis of $\eta^6$-naphthalene complexes.* $C_{10}H_8Cr(CO)_3$ (**1**) was prepared by a reaction analogous to that described by *Pauson* [5] for monocyclic (arene)tricarbonylchromium compounds. The procedure was modified to take account of the lability of the naphthalene ligand in coordinating solvents [6].

$$C_{10}H_8Cr(CO)_3 + 3\,THF \rightleftharpoons (THF)_3Cr(CO)_3 + C_{10}H_8$$

The synthesis of the complexes $C_{10}H_8Cr(PF_3)_3$ (**2**), $C_{10}H_8Cr[P(OMe)_3]_3$ (**3**), $(C_{10}H_8)_2Cr$ (**4**), and $C_{10}H_8Cr(PMe_3)_3$ (**5**) has been described in [1].

$C_{10}H_8Cr(PF_2OMe)_3$ (**6**) was obtained unexpectedly when the phosphite complex **3** was treated with hydrofluoroboric acid. The basicity of compounds of the type $\eta^nC_nH_nM[P(OR)_3]_m$ (*e.g.* n=5, M=Co, m=2 or n=6, M=Ru, m=2) is well documented [7]; they react with *Lewis* acids *via* addition and formation of M,H-, M,C- or M,M'-bonds. Thus, not complex **6** but $\{C_{10}H_8CrH[P(OMe)_3]_3\}^+BF_4^-$ was expected from this reaction. This product was not observed; instead, reaction of **3** with one equivalent of $HBF_4$ in ether solution yielded a mixture of compounds of composition $C_{10}H_8Cr[PF_n(OMe)_{3-n}]_3$ (n=0, 1 and 2). With an excess of $HBF_4$ this reaction was very rapid in methylene chloride even at $-30°$, and compound **6** was the only product isolated. Complex **6** forms red air-stable crystals which melt at $87 \pm 1°$.

$$C_{10}H_8Cr[P(OMe)_3]_3 \xrightarrow[CH_2Cl_2]{HBF_4,\ -30°} C_{10}H_8Cr(PF_2OMe)_3\ (\mathbf{6})$$

The transformation of $P(OMe)_3$ to $PF_2OMe$ in the metal coordination sphere has been inferred from volumetric and IR. studies of the reaction of several iron and nickel phosphite complexes with $BF_3$ gas [8]. The complexes were not isolated in this study. Alternatively, mixed methyl fluorophosphite compounds result from the reaction of coordinated $PF_3$ with methanol under basic conditions [9] [10]. Given the readily accessible and easily manipulated reagents and starting materials, the reaction with $HBF_4$ provides an attractive alternative to previous synthetic routes for this class of compounds.

Table 1. *$^{13}$C-NMR. chemical shifts*[a]) *of $\eta^6$-naphthalene chromium (O) complexes*

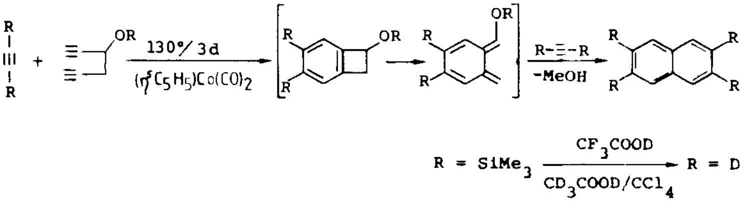
| Compound | C(6,7)[b]) | C(5,8) | C(4a,8a) | C(1,4) | C(2,3) | C(L) |
|---|---|---|---|---|---|---|
| $C_{10}H_8$[c]) | 125.9 | 128.1 | 133.7 | 128.1 | 125.9 | |
| $C_{10}H_8Cr(CO)_3$ (**1**) | 92.3 | 90.7 | 105.8 | 128.8 | 128.4 | 228.7 (CO) |
| $C_{10}H_8Cr(PF_3)_3$ (**2**) | 87.7 | 86.7 | 102.3 | 129.6 | 128.2 | |
| $C_{10}H_8Cr(PF_2OMe)_3$ (**6**) | 84.8 | 82.8 | 100.4 | 130.2 | 127.1 | 52.1 $PF_2OMe$ |
| $C_{10}H_8Cr(P(OMe)_3)_3$ (**3**) | 80.5 | 78.0 | 99.1 | 131.4 | 123.4 | 51.2 $P(OMe)_3$ |
| $(C_{10}H_8)_2Cr$ (**4**) | 77.8 | 75.0 | [d]) | 133.9 | 123.1 | |
| $C_{10}H_8Cr(PMe_3)_3$ (**5**) | 75.7 | 72.3 | 97.3 | 131.5 | 121.5 | 24.9 $PMe_3$ |
| $[C_{10}H_8Fe(\eta^5\text{-}C_5H_5)]^+$ (**7**)[e]) | 87.7 | 86.1 | 96.9 | 133.1 | 131.8 | 77.3 ($C_5H_5$) |

[a]) Measured in $C_6D_6$; chemical shifts are positive downfield relative to TMS. [b]) Numbering system see *Figure 2.* [c]) Measured in $CDCl_3$; the band assignment was taken from [11] and confirmed from our spectrum of (2,3,6,7-$^2H_4$)-naphthalene. [d]) Not observed because of low solubility of the compound. [e]) Values from [12]. Measured in $CD_3CN$.

*$^{13}$C-NMR. spectra of naphthalene complexes.* Apart from lines associated with solvent ($C_6D_6$) and coligands, the proton-decoupled $^{13}$C-NMR. spectra of the naphthalene complexes consist of five resonances. The chemical shifts and assignments are listed in *Table 1*, together with the data for free naphthalene and for $[C_{10}H_8FeC_5H_5]^+ [PF_6]^-$ (**7**) which are included for comparison. Assignments are made on the basis of chemical shift differences (C(1-4) *vs.* C(5-8)) and intensity of bands (C(4a),C(8a)). Complex **3** was selected to establish the sequence of C($\alpha$)- and C($\beta$)-resonances (C(1,4) *vs.* C(2,3) and C(5,8) *vs.* C(6,7)) in the two rings. Off resonance experiments indicated that in the uncomplexed ring C($\alpha$)-atoms resonate at higher frequency than C($\beta$)-atoms, a situation equal to that found in free naphthalene. For the C-atoms of the complexed ring, however, the order appeared to be reversed. This was all the more puzzling as a recent assignment of $^{13}$C-NMR. bands in **1** based on similar NMR. techniques was at variance with our results for **3** in this respect [13]. An unambiguous solution to this problem was sought, and we undertook the synthesis of the [2,3,6,7-$^2H_4$]-naphthalene complexes $d^4$-**3** and $d^4$-**1**.

The $d^4$-naphthalene was prepared using the cobalt catalyzed acetylene trimerization reaction reported by *Vollhardt & Funk* [14] *(Scheme 1)*. The complexes $C_{10}H_4{}^2H_4Cr(CO)_3$ ($d^4$-**1**) and $C_{10}H_4{}^2H_4$ $Cr[P(OMe)_3]_3$ ($d^4$-**3**) were then prepared as described above. The decrease in intensity of the $^{13}$C-NMR. resonances *(Fig. 1)* associated with the deuteriated C-atoms confirmed our assignment. The same

*Scheme 1*



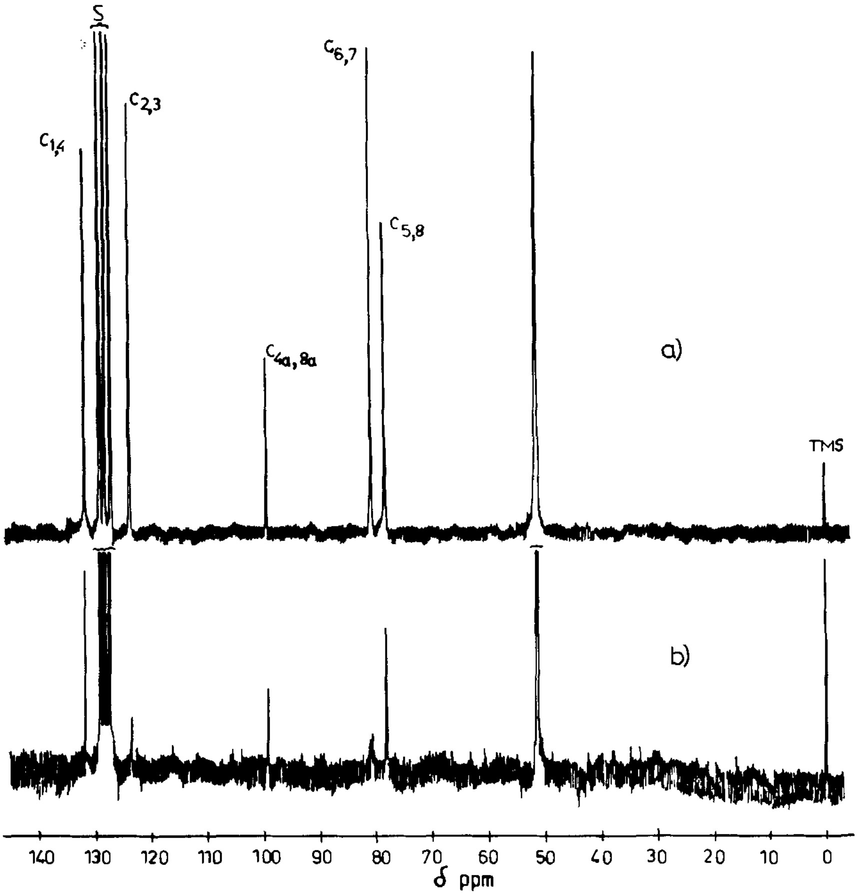


Fig. 1. *Proton decoupled* $^{13}$*C-NMR. spectra* (in $C_6D_6$) *of* a) *$(\eta^6$-$C_{10}H_8)Cr[P(OMe)_3]_3$ and* b) *$(\eta^6$-$C_{10}H_4[2,3,6,7$-$^2H_4])Cr[P(OMe)_3]_3$*

sequence was also found for **1**, thus necessitating a reappraisal of earlier data [13]. In all complexes of this series the metal coordinates to one ring of the naphthalene. At 35° (temperature of the NMR. probe) there is no migration of the chromium from one ring to the other. Further investigation of this coordination stability was carried out, and we recorded the $^1$H-NMR. spectrum of the sandwich complex **4** at elevated temperatures. In $C_6D_6$ we found that there was no change of the spectrum up to 130°: thus, we observed the complex to be inert to inter- and intramolecular ring exchange even at this temperature.

Coordination of an arene to a transition metal causes large shifts to lower frequencies of the ring C-resonances in respect to the free arene [15]. The increase in shielding has been variously attributed to metal ligand bond anisotropy [16–18], changes in ring C-hybridization [19] and changes in electron density in the $\sigma$- [20] [21] and $\pi$- [22–25] system of the coordinated arene. A coherent theoretical

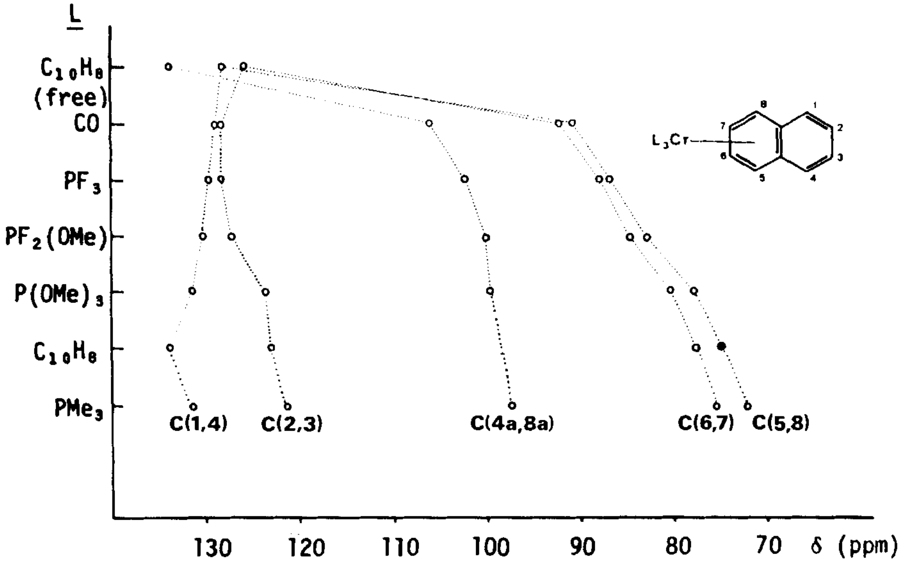


Fig. 2. *Schematic representation of naphthalene $^{13}C$-NMR. chemical shifts of* $(\eta^6\text{-}C_{10}H_8)CrL_3$ *complexes*

interpretation of these shifts is not yet available [26] [27], however, a thorough study of the factors that influence the coordination shift concludes that changes in $\pi$-electron density and, particularly, metal to arene $\pi^*$-backbonding play a dominant role in the observed shielding of coordinated arenes [23]. These conclusions receive support from the results of molecular orbital calculations [25] [28-30] and a He(I) photoelectron study [31]. Thus, although $^{13}C$-NMR.-shift differences in metal-arene complexes cannot be equated with the extent of $\pi^*$-backbonding, they do seem to indicate the same trend. Substitution of a $PPh_3$ ligand for a CO in (benzene)tricarbonylchromium results in an increased shielding of the ring C-atoms [32]. This has been attributed to the larger $\sigma$-donor/$\pi$-acceptor ratio of the phosphine compared to CO, which thereby raises the HOMO of the $CrL_3$ group and facilitates metal to arene backbonding. The opposite effect is observed for CO substitution by CS, in agreement with the stronger $\pi$-acidity of the thiocarbonyl ligand [33]. In the present series of six compounds the trend is more pronounced because of the absence of the electronic buffering effect of the carbonyl ligand.

Our $^{13}C$-NMR. data for naphthalene complexes is presented graphically in *Figure 2.* The smallest coordination shifts are observed for the complex with the strong acceptor group $Cr(CO)_3$. With increasing donor characteristics of the co-ligands, the coordinated C-resonances are found to undergo a smooth transition to higher field. The regularity of this trend is exemplified in complex **6**, the resonances of which can be predicted to within 1 ppm from the weighted average of the shifts of the $PF_3$ and $P(OMe)_3$ analogues. Complex **5**, containing the powerful donor fragment $Cr(PMe_3)_3$ terminates the series. Its $^{13}C$-resonances are shifted up to 18.4 ppm upfield from those of the carbonyl complex **1**. Naphthalene itself exerts an influence intermediate between three trimethylphosphites and trimethylphosphines. The sandwich compound is thus to be classified amongst very electron-rich complexes. The resonances of the uncomplexed ring C-atoms experience much smaller shifts and remain in the aromatic region. Their variation is considerable, however, in individual compounds. The sometimes large difference between C($\alpha$)-atoms which experience downfield shifts and C($\beta$)-atoms which undergo upfield shifts on coordination of the other ring are particularly striking.

The correlation between $^{13}$C-NMR. arene-coordination shift and donor/acceptor property of the coligand is remarkable. It would seem probable that this correlation can be extended to the reactivity of the metal-arene bond and to that of the coordinated naphthalene. Supportive evidence for the former is based on the observation of a large increase in lability of the chromium-naphthalene bond in complexes containing donor coligands and in the increased sensitivity towards oxidation of these compounds [1]. In order to test the hypothesis of a correlation of $^{13}$C-NMR. shifts with naphthalene reactivity, we compared the reactions of complexes **1-4** and **6-7** with carbanions.

*Nucleophilic substitution for hydride on coordinated naphthalene.* The addition of ester, nitrile and sulfur stabilized carbanions to (arene)tricarbonylchromium has been shown to yield anionic cyclohexadienyl complexes which, on oxidation, afford substituted arenes in high yield. Scope and mechanism of this direct alkylation of unfunctionalized aromatic rings have been primarily investigated by *Semmelhack et al.* [2] [34]. In a recent publication 2-methylpropionitrile carbanion was reported to add to the $\alpha$-position in (naphthalene)tricarbonylchromium [35]. This regioselectivity appears to be general.

Sequential treatment of **1** with carbanions and iodine or Ce(IV)-salt at low temperature affords the $\alpha$-substituted naphthalenes in fair to excellent yields. The results are listed in *Table 2*. The $PF_3$-compound **2** is found to react correspondingly; this is not unexpected as the close resemblance between the two ligands CO and $PF_3$ is well documented [36]. The anion prepared from 2-methylpropionitrile also reacts with **6** to afford after oxidation 1-(2-cyanoisopropyl)naphthalene. Contrasted

*Scheme 2*

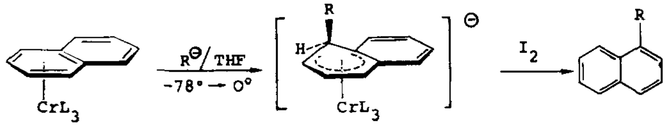


Table 2. *Nucleophilic aromatic substitution for $H^-$ in naphthalene $CrL_3$ complexes*

| Nucleophile | Yields of $\alpha$-substituted naphthalene (%) | | | | |
|---|---|---|---|---|---|
| LiR | L=CO | $PF_3$ | $PF_2OMe$ | $P(OMe)_3$ | $L_3=C_{10}H_8$ |
| $LiCMe_2CN$ | 96 | 90 | 78 | < 3 | 0 |
| $LiCH_2CN$ | 54 | 55 | | | |
| $LiCHS(CH_2)_3S$ | 83 | | | | |
| LiOMe | 30 | | | | |

to this, analogous reactions with the $P(OMe)_3$-complex **3** and the sandwich-compound **4** failed to yield more than traces of substituted naphthalene. Changes in reaction temperature (−78 to 0°) and time did not alter this result. Addition of benzylbromide to a mixture of complex **3** and 2-lithio-2-methylpropionitrile at −20° results in recovered starting complex and $\alpha,\alpha$-dimethyl-$\beta$-phenyl-propionitrile and this suggests that the complex **3** fails to react with the carbanion. An alternative explanation would involve the transfer of the carbanion from a labile anionic intermediate complex to the electrophile - a reaction observed in (arene)tricarbonylchromium [34]. The negative results of our attempts to trap such an intermediate by oxidation under various conditions, as well as the striking contrast to the behaviour of the CO, $PF_3$ and $PF_2OMe$ complexes, lends weight to the first interpretation.

Our results indicate, therefore, that nucleophilic substitution reactions on the coordinated naphthalene requires strongly electron-attracting coligands with a $\sigma$-donor/$\pi$-acceptor ratio smaller than or equal to $PF_2OMe$. Inspection of *Table 1* shows that these same complexes have the smallest $^{13}C$-NMR. arene-coordination shifts. The coordinated ring C-atoms of the $PF_2OMe$ complex **6** resonate at 82.8 and 84.8 ppm; thus, any naphthalene complex exhibiting resonances at or above these values should be susceptible to attack by the stabilized carbanions used in this study. Confirmation of the correlation rests, so far, on a single example. The complex **7** with the cationic iron-naphthalene component, first synthesized by *Nesmeyanov* [37], exhibits coordinated ring $^{13}C$-NMR. resonances [12] which are virtually identical to those of the $PF_3$ complex **2** *(Table 1)*. Complex **7** reacts readily with 2-lithio-2-methyl-propionitrile in THF at −78°. Oxidation of the neutral cyclohexadienyl intermediate with Ce(IV)-salt affords the $\alpha$-substituted naphthalene. The yield is moderate (55%). It is our impression that this is due to the second step - hydride abstraction and removal of the organic ligand from the metal - rather than to the reaction of the complex with the nucleophile. This is a problem which certainly merits further consideration.

We wish to express our thanks to Mr. *J. P. Saulnier* for careful NMR. measurements.

## Experimental Part

$^1H$- and $^{13}C$-NMR. spectra were recorded on a *Varian* XL-100 spectrometer operating at 100.1 and 25.2 MHz, respectively. All chemical shifts are reported in ppm downfield from TMS. IR. spectra were recorded on a *Pye Unicam* SP-1100 spectrometer. Mass spectra were measured on a *Varian* CH-4 spectrometer at 70 eV. Melting points were obtained in sealed capillaries on a *Büchi* 510 apparatus and are not corrected. All preparations involving organometallic complexes were carried out in freshly distilled, dry, deoxygenated solvents in an atmosphere of dry nitrogen or argon.

*Synthesis of naphthalene complexes.* The compounds $C_{10}H_8CrL_3$ (L = $PF_3$ (**2**), $P(OMe)_3$ (**3**) and $PMe_3$ (**6**)) were prepared by arene displacement reactions from the sandwich complex $(C_{10}H_8)_2Cr$ (**4**) as described previously [1]. $[C_{10}H_8FeC_5H_5]^+ PF_6^-$ (**7**) was synthesized from ferrocene according to the methods reported by *Hendrickson* [12] and *Lee* [38]. $C_{10}H_8Cr(CO)_3$ (**1**) [39] was prepared by a slightly modified procedure to that described by *Pauson* for monocyclic (arene)tricarbonylchromium compounds [5]: A mixture of naphthalene (5.3 g, 42 mmol) and $Cr(CO)_6$ (4.4 g, 20 mmol) were refluxed in dibutylether (100 ml)/THF (1 ml) for 70 h under $N_2$. The heating bath was maintained at 160° for 15 h and at 145° for the remaining time. Solvent and excess naphthalene were removed *in vacuo*. Extraction with toluene, filtration and crystallization from toluene/hexane at $-78°$ yielded **1** (4.2 g, 80%).

*$C_{10}H_8Cr(PF_2OMe)_3$* (**6**). A solution of $HBF_4$ (3 ml, ~54% in ether) in $CH_2Cl_2$ (5 ml) was added dropwise to a solution of the phosphite complex **3** (1.3 g, 2.4 mmol) in $CH_2Cl_2$ (10 ml) at $-78°$. Upon addition of the acid an immediate colour change from dark brown to bright red was observed. The solution was left to warm up to 0° (30 min), recooled to $-78°$ and treated with pyridine (3 ml). The mixture was filtered at room temperature, taken to dryness and the residue extracted with hexane. Filtration on degassed kieselgur and crystallization at $-78°$ yielded red crystals of **6** (620 mg, 54%). - $^1$H-NMR. ($C_6D_6$): 7.28 (*m*, 2 H); 6.94 (*m*, 2 H); 5.56 (*m*, 2 H); 4.87 (*m*, 2 H); 3.37 (*m*, 9 H). - MS.: 480 ($M^+$), 380 ($M^+ - PF_2OMe$), 280 ($M^+ - 2PF_2OMe$), 180 (100%, $M^+ - 3PF_2OMe$), 128, 100, 52.

*$C_{10}H_4[2,3,6,7\text{-}^2H_4]CrP(OMe)_3]_3$* ($d^4$-**3**) was prepared and purified as described for the non-deuteriated compound. The intermediate sandwich complex ($d^4$-**4**) was not isolated. Chromium (*ca.* 60 mg, 1.1 mmol) was evaporated into a solution of naphthalene-$d^4$ (600 mg, 4.5 mmol) in diglyme (30 ml) in a rotating solution metal atom reactor [40]. Filtration of the resulting brown-red solution and treatment with $P(OMe)_3$ (1 ml) yielded ($d^4$-**3**) (175 mg, 29%).

*Reactions with nucleophiles.* - a) *With 2-lithio-2-methylpropionitrile.* The generation of the anion and the reaction conditions were chosen analogous to those described by *Semmelhack et al.* [34] for reactions with (benzene)tricarbonylchromium. A solution of lithium isopropylamide (LDA) in THF was prepared from freshly distilled isopropylamine (150 mg, 1.5 mmol) and butyllithium (0.95 ml of 1.6 m solution in hexane) in THF (5 ml) at 0°. After 20 min the solution was cooled to $-78°$ and 2-methylpropionitrile (104 mg, 1.5 mmol) was added rapidly dropwise *via* a syringe. Stirring was continued at 0° for 30 min. Dropwise addition of a cold solution of complex **1** (396 mg, 1.5 mmol) in THF (10 ml) to this mixture at $-78°$ was followed by warming up to 0° (30 min), recooling and treatment at $-78°$ with iodine (2 g in 10 ml THF). The reaction mixture was left to warm-up overnight. THF was removed *in vacuo*, the crude product taken up in ether (30 ml) and washed sequentially with aq. $NaHSO_3$-solution (10%, 2× 10 ml), 2N HCl (10 ml), sat. $NaHCO_3$-solution (2× 10 ml), water (2× 10 ml) and brine (10 ml). The organic phase was dried and ether was removed in a rotary evaporator. The yellow viscous oil was chromatographed on silica gel (chloroform/hexane 2:3) to yield 2,2-dimethyl-α-naphthylacetonitrile [41] (0.280 g, 96%). IR. and $^1$H-NMR. spectra of the compound were identical to those of the compound prepared *via* double methylation of α-naphthylacetonitrile by published methods [35] [41].

Analogous reactions of 2-lithio-2-methylpropionitrile with complexes **2** and **6** yielded the α-substituted naphthalene in 90 and 78% yield respectively.

The cationic iron complex **7** ($PF_6^-$-salt), insoluble in cold THF, was added as a solid to the cold ($-78°$) solution of the anion in THF. Upon addition of the orange-brown complex **7** (394 mg, 1 mmol), the reaction mixture turned dark green, indicating rapid reaction. The homogeneous solution was left at $-40°$ for 30 min, recooled to $-78°$ and treated with a solution of $Ce(NH_4)_2(NO_3)_6$ (1.5 g) in THF. Work-up in the usual manner yielded 2,2-dimethyl-α-naphthylacetonitrile (71 mg, 55%).

Reactions with the chromium complexes **3** and **4**. As before, complexes **3** (THF solution) and **4** (solid) were added to the cold carbanion solution. After oxidative work-up ($I_2$ or Ce(IV)-salt) only unsubstituted naphthalene was isolated. In additional experiments, the solutions containing the anion and complex **3** were left at $-70$, $-40$ and 0° for periods of 0.5, 0.5 and 15 h respectively, followed by $I_2$ or Ce(IV)-salt addition at $-78°$. In all experiments naphthalene was recovered almost quantitatively; traces of substituted naphthalene were observed in the $-40°$ reaction. *Under addition of benzylbromide.* A mixture of **3** (470 mg, 0.851 mmol) and 2-lithio-2-methylpropionitrile (1 mol-equiv.) was prepared as described above and brought to $-20°$ (20 min). The solution was recooled to $-78°$ and benzylbromide (145 mg, 0.851 mmol) was added *via* a syringe. The mixture was taken to dryness, dissolved in ether, filtered and analyzed by $^1$H-NMR. (in $C_6D_6$). The product consisted of starting complex, free naphthalene and β-dimethylpropionitrile. The latter was isolated in 55% yield from this mixture.

b) *Reactions with lithioacetonitrile.* Preparation of the anion, reaction with complexes **1** and **2** as well as work-up of the reaction mixtures were executed on a similar scale exactly analogous to the procedure described above for reactions with 2-lithio-2-methylpropionitrile. The crude products were purified by chromatography on silica gel (toluene). $\alpha$-Acetonitrilenaphthalene was isolated in 54 and 55% yields respectively. The IR. and $^1$H-NMR. spectra were identical to those of a commercial sample of the compound.

c) *Reaction of* **1** *with 2-lithio-1,3-dithiane.* The carbonyl complex **1** (1.06 g, 4 mmol) was added at $-78°$ to a solution of 2-lithio-1,3-dithiane [42] in THF (10 ml) prepared from freshly sublimed 1,3-dithiane (480 mg, 4 mmol) and butyllithium (2.5 ml of 1.6M solution in hexane). As before, the reaction mixture was left to warm-up to 0° (30 min) before treating it with $I_2$ at $-78°$. Work-up in the usual manner (described above) and recrystallization of the crude product from methanol yielded 2-($\alpha$-naphthyl)-1.3-dithiane [43] as colourless crystals, m.p. 141-142°, yield 820 mg (83%). - IR. ($CCl_4$, $cm^{-1}$): 3060*m*, 3050*m*, 2960*s*, 2940*s*, 2850*m*, 2830*m*, 2810*m*, 1600*m*, 1515*m*, 1455*s*, 1420*m*, 1400*m*, 1280*s*, 1270*s*, 1100 br., 1060*s*, 1020 br., 910*m*. - $^1$H-NMR. ($CDCl_3$): 8.36 (*m*, 1 H); 7.42-7.96 (*m*, 6 H); 5.97 (*s*, 1 H); 2.88-3.44 (*m*, 4 H); 2.18 (*m*, 2 H). - MS.: 246 (70), 172 (70), 171 (100).

*Conversion to $\alpha$-naphthaldehyde.* A solution of 2-($\alpha$-naphthyl)-1,3-dithiane (246 mg, 1 mmol) in acetonitrile (2 ml) was added at $-5°$ to a solution of *N*-bromosuccinimide (1.07 g, 6 mmol) in 20 ml of acetonitrile/water 4:1. Stirring was continued from $-5°$ to 30°. Work-up as described by *Corey* [44] followed by distillation afforded $\alpha$-naphthaldehyde in quantitative yield. The IR. and $^1$H-NMR. data were identical to those of a commercial sample of the compound.

d) *Reaction of* **1** *with lithiummethoxide.* Complex **1** (460 mg, 1.75 mmol) was added as a solid to a solution of MeOLi (75 mg, 2 mmol) in THF (5 ml) and HMPA (2 ml) at $-78°$. Proceeding as described above for the reaction of **1** with 2-lithio-2-methylpropionitrile followed by chromatography of the crude product on silica gel (hexane) yielded 1-methoxynaphthalene (80 mg, 30%).

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