# Dicarbonylnitrosylchromium Complexes of Methylbenzenes and Methylcyclohexadienyls

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The complexes [Cr(CO)$_3$L] (I; L = C$_6$H$_n$Me$_{6-n}$, $n$ = 0—2) react with [NO][PF$_6$] in methanol–toluene, nitromethane, or liquid sulphur dioxide to afford [Cr(CO)$_2$(NO)L][PF$_6$], (II). These cations react with nucleophiles such as H$^-$, D$^-$, or Me$^-$ to give neutral cyclohexadienyl complexes [Cr(CO)$_2$(NO)L] (III; L = C$_6$H$_{n+1}$Me$_{6-n}$) by *exo*-attack at the co-ordinated arene.

ALTHOUGH the chemistry of organometallic nitrosyls has been little studied,[1-3] we believe it is of great interest for two reasons. First, it is well established that intramolecular electron transfer may occur in transition-metal nitrosyl complexes *via* interconversion of the linear (NO$^+$) and bent (NO$^-$) arrangements of the nitrogen monoxide ligand.[4] As such electron transfer may occur in processes involving nitrosyl complexes as catalysts, it is possible that a comparison of the properties of related organometallic carbonyl and nitrosyl complexes may afford information as to the involvement of the NO$^+$–NO$^-$ interconversion in catalytic systems. Secondly, whereas many cationic organometallics are generated in reactions which involve modification of the organic ligand present in a neutral precursor, carbonyl-displacement reactions of NO$^+$ allow cationic organometallic nitrosyls to be prepared in which the organic ligand is unmodified. Thus, for a given neutral starting material, the use of methods such as hydride abstraction or protonation may lead to species which differ from those afforded by NO$^+$ reactions and therefore to different organic products on reaction with nucleophilic reagents.

TABLE 1

I.r., analytical, m.p., and conductance data for the complexes [Cr(CO)$_2$(NO)L][PF$_6$], (II), and [Cr(CO)$_2$(NO)L], (III)

| Complex | L | M.p. ($\theta_c$/°C) | Yield/ % | Analyses [a]/% C | H | N | $\bar{\nu}$(CO) / cm$^{-1}$ | $\bar{\nu}$(NO) / cm$^{-1}$ | Medium | $\Lambda$ [b] / S cm$^2$ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| (II) | Me$_6$C$_6$ | decomp. >170 | 62 [c] | 37·6 (37·8) | 4·1 (4·1) | 2·9 (3·2) | 2 065, 2 016 | 1 758 | CH$_2$Cl$_2$ | 157 |
| (II) | Me$_5$HC$_6$ | decomp. >165 | 53 [c] | 35·4 (36·2) | 3·7 (3·8) | 3·4 (3·3) | 2 069, 2 022 | 1 760 | CH$_2$Cl$_2$ | 144 |
| (II) | 1,2,3,4-Me$_4$H$_2$C$_6$ | decomp. >155 | 17 | 34·3 (34·5) | 3·5 (3·4) | 3·7 (3·4) | 2 073, 2 027 | 1 763 | CH$_2$Cl$_2$ | 159 |
| (II) | 1,2,3,5-Me$_4$H$_2$C$_6$ | decomp. >135 | 14 | 34·4 (34·5) | 3·4 (3·4) | 3·3 (3·4) | 2 073, 2 025 | 1 761 | CH$_2$Cl$_2$ | 131 |
| (II) | 1,2,4,5-Me$_4$H$_2$C$_6$ | decomp. >185 | 21 | 34·4 (34·5) | 3·3 (3·4) | 3·4 (3·4) | 2 072, 2 027 | 1 764 | CH$_2$Cl$_2$ | 163 |
| (III) | *endo*-Me$_6$HC$_6$ | 101 | 20 | 56·2 (55·8) | 6·6 (6·4) | 4·5 (4·6) | 2 005, 1 948 | 1 686 | hexane | |
| (III) | Me$_5$H$_2$C$_6$ | 83 | 15 | 54·3 (54·3) | 5·9 (6·0) | 4·8 (4·9) | 2 005, 1 948 | 1 685 | hexane | |
| (III) | 1,2,3,4-Me$_4$H$_3$C$_6$ | 25 [d] | 55 | 52·6 (52·7) | 5·4 (5·5) | 5·2 (5·1) | 2 009, 1 954 | 1 688 | hexane | |
| (III) | 1,2,3,5-Me$_4$H$_3$C$_6$ | 52 | 20 | 52·8 (52·7) | 5·8 (5·5) | 5·2 (5·1) | 2 007, 1 949 | 1 691 | hexane | |
| (III) | 1,2,4,5-Me$_4$H$_3$C$_6$ | 50 | 45 | 52·5 (52·7) | 5·6 (5·5) | 5·1 (5·1) | 2 009, 1 951 | 1 692 | hexane | |

[a] Calculated values are given in parentheses. [b] 10$^{-4}$M In acetone. [c] From reaction in SO$_2$. [d] Solid below room temperature.

We therefore began a study of the preparation and reactions of organometallic nitrosyls with a view to investigating the effects of the nitrosyl ligand on the reactions of organometallic complexes and now report details of the chemistry of [Cr(CO)$_2$(NO)L][PF$_6$] (L = $\eta$-arene). These species not only react with nucleophiles such as H$^-$, D$^-$, or Me$^-$, but are isoelectronic with the known cations [Mn(CO)$_3$L]$^+$ and thus allow a comparison to be made between isoelectronic carbonyl and nitrosyl organometallics.

## RESULTS

*Synthetic Studies*.—The $\eta$-methylbenzene complexes, [Cr(CO)$_3$L], (I), reacted with [NO][PF$_6$] in a variety of solvents to afford [Cr(CO)$_2$(NO)L][PF$_6$] (II; L = C$_6$H$_n$Me$_{6-n}$, $n$ = 0—2). These complexes, characterised by i.r. and n.m.r. spectroscopy, elemental analysis, and conductivity measurements (Tables 1 and 2) are yellow air-stable crystalline solids which dissolve in polar solvents such as acetone, CH$_2$Cl$_2$, and acetonitrile to give yellow, moderately stable, solutions. In methanol–toluene mixtures, widely used as a solvent for [NO][PF$_6$] reactions, the cations (II) were isolated in yields which rapidly decreased as methyl substitution in the arene decreased. The 1,3,5-trimethylbenzene and 1,2,3,4-tetrahydronaphthalene (thn) analogues were only isolated in quantities sufficient for i.r. identification [*i.e.* in CH$_2$Cl$_2$ $\bar{\nu}$(CO) = 2 073 and 2 027, $\bar{\nu}$(NO) = 1 763 (L = C$_6$H$_3$Me$_3$); $\bar{\nu}$(CO) = 2 077 and 2 033, $\bar{\nu}$(NO) = 1 765 cm$^{-1}$ (L = thn)]. The salts were precipitated from the reaction mixture, either during the reaction or on subsequent addition of diethyl ether, and it is noteworthy that the mother liquors, after filtration, were deep red. The colour of these solutions is reminiscent of that of the cyclohexadienyl derivatives described below and it is therefore possible that such species occur as by-products in the salt preparations. Attempts to isolate complexes from the red solutions proved fruitless, although some

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[4] C. P. Brock, J. P. Collman, G. Dolcetti, P. H. Farnham, J. A. Ibers, J. E. Lester, and C. A. Reed, *Inorg. Chem.*, 1973, **12**, 1304.

evidence for the presence of other carbonyl-containing species was gained. When the reaction between (I; L = $C_6Me_6$) and [NO][$PF_6$] was carried out in ethanol–toluene, hexane addition afforded a red-brown solid which, in $CH_2Cl_2$, showed i.r. absorptions due to (II; $n = 0$) plus others at 2 050, 1 960, and 1 730 $cm^{-1}$. This second set of peaks occurred at lower wavenumber than that of the salt and it is possible that it is due to a cyclohexadienyl chromium complex. The absorptions are, however, still relatively high in wavenumber for a neutral species and the suggested presence of such a cyclohexadienyl must therefore be viewed with caution. Attempted isolation of the complex failed.

In attempts to find a solvent system which would give higher yields of the salts, we found that in nitromethane the cations were generated in quantities similar to those formed in methanol–toluene, and that (II; $n = 0$) may be isolated from the reaction of (I; L = $C_6Me_6$) with [NO][$PF_6$] in concentrated sulphuric acid. The most useful solvent for the preparation of the cationic nitrosyls, however, appears to be liquid sulphur dioxide. As some indication of the utility of this solvent, the yield of (II; $n = 1$) was increased from 20% in methanol–toluene to 50% in liquid $SO_2$ and even (II; $n = 5$) [$\bar{\nu}$(CO) = 2 079 and 2 033, $\bar{\nu}$(NO) = 1 771 $cm^{-1}$] was isolated in quantities sufficient for i.r. identification. The final solvent used, acetonitrile, has already been reported as yielding [$Cr(NO)_2(NCMe)_4$][$PF_6$]$_2$.[5]

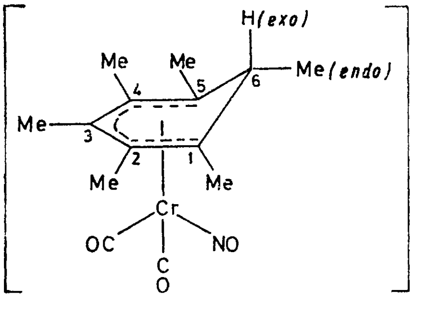
TABLE 2

$^1$H N.m.r. spectra ($\tau$) of complexes (II) [a]

| L | Methyl protons [b] | Ring protons [b] |
|---|---|---|
| $Me_6C_6$ | 7·52(18) [c] | |
| $Me_5HC_6$ | 7·61(6), 7·57(6), 7·47(3) | 3·45(1) |
| 1,2,3,4-$Me_4H_2C_6$ | 7·58(6), 7·51(6) | 3·39(2) |
| 1,2,3,5-$Me_4H_2C_6$ | 7·65(3), 7·60(3), 7·49(6) | 3·51(2) |
| 1,2,4,5-$Me_4H_2C_6$ | 7·65(12) | 3·19(2) |

[a] In $CD_3NO_2$. [b] All signals were singlets. [c] Intensities are given in parentheses.

Addition of $H^-$, as $NaBH_4$, to tetrahydrofuran (thf) suspensions of the nitrosyl cations resulted in formation of red solutions containing the corresponding cyclohexadienyl derivatives, (III; L = $C_6H_{n+1}Me_{6-n}$). Evaporation of the filtered reaction mixture followed by chromatography on basic alumina afforded a red band which, in certain cases, contained a mixture of isomeric cyclohexadienyl species. The predominant isomer formed was that which results from *exo*-attack of the nucleophile at an unsubstituted carbon atom of the arene ring. The minor products, which were always eluted from the chromatography column first, were those in which attack by $H^-$ occurred at a methyl-substituted carbon atom. In no case did reaction at the co-ordinated nitrosyl or carbonyl ligand take place. After elution of the minor products, the predominant isomer in each case was crystallised from hexane, and characterised by i.r. and n.m.r. spectroscopy and elemental analysis (Tables 1 and 3). Each of the cyclohexadienyl complexes (III; $n = 0$—2) is an orange-red crystalline solid [(III; L = 1,2,3,4-$Me_4H_3C_6$) is a liquid at room temperature] soluble in polar solvents to give orange solutions which are rapidly decomposed by air. The mass spectrum of each of the complexes exhibited sequential loss of two carbonyl and one nitrosyl ligands followed by loss of the organic ring.



(III) L = *endo*-$Me_6HC_6$

TABLE 3

$^1$H N.m.r. spectra ($\tau$) of complexes (III) [a]

| L | Methyl protons [b] 1,5 | 2,4 | 3 | 6(*endo*) | Arene protons [b] 1,5 | 2,4 | 3 | 6 |
|---|---|---|---|---|---|---|---|---|
| *endo*-$Me_6HC_6$ | 8·73 (s, 6) | 8·34 (s, 6) | 7·92 (s, 3) | 9·04 (d, 3) [c] | | | | 7·89 (qt, 1) [c] |
| *endo*-$Me_6DC_6$ | 8·73 (s, 6) | 8·36 (s, 6) | 7·92 (s, 3) | 9·06 (s, 3) | | | | |
| $Me_5H_2C_6$ | 8·61 (s, 6) | 8·39 (s, 6) | 7·92 (s, 3) | | | | | 8·00 (irreg. d, 2) |
| *exo*-$Me_5DHC_6$ | 8·60 (s, 6) | 8·38 (s, 6) | 7·90 (s, 3) | | | | | 8·06 (brd. s, 1) |
| 1,2,3,4-$Me_4H_3C_6$ | 8·57 (s, 3) | 8·41 (ss, 6) | 7·93 (s, 3) | | 7·62 (dd, 1) [d] | | | 8·06 (irreg. d, 2) [e] |
| *exo*-1,2,3,4-$Me_4DH_2C_6$ | 8·60 (s, 3) | 8·44 (ss, 6) | 7·96 (s, 3) | | 7·65 (d, 1) [e] | | | 8·08 (d, 1) [e] |
| 1,2,3,5-$Me_4H_3C_6$ | 8·75 (s, 3) [f]<br>8·61 (s, 3) | 8·45 (s, 3) | 7·94 (s, 3) | | | 5·53 (s, 1) | | 8·07 (brd. s, 2) |
| *exo*-1,2,3,5-$Me_4DH_2C_6$ | 8·75 (s, 3) [f]<br>8·61 (s, 3) | 8·45 (s, 3) | 7·95 (s, 3) | | | 5·54 (s, 1) | | 8·10 (brd, s, 1) |
| 1,2,4,5-$Me_4H_3C_6$ | 8·72 (s, 6) | 8·51 (s, 6) | | | | | 5·01 (s, 1) | 7·96 (irreg. d, 2) |
| *exo*-1,2,4,5-$Me_4DH_2C_6$ | 8·71 (s, 6) | 8·50 (s, 6) | | | | | 5·03 (s, 1) | 8·02 (brd. s, 1) |

[a] In $C_6D_6$. [b] Multiplicity and intensity are given in parentheses; s = singlet, ss = two barely resolved singlets, d = doublet, qt = quartet, brd. s = broad singlet (unresolved coupling), and irreg. d = irregular doublet. [c] 7 Hz Coupling. [d] 5 Hz Coupling between $H_1$ and *endo*-$H_6$; 2 Hz coupling between $H_1$ and *exo*-$H_6$. [e] 5 Hz Coupling between $H_1$ and *endo*-$H_6$. [f] $\tau$ 8·75 May be assigned to $Me_5$ and $\tau$ 8·61 to $Me_1$.

Reaction of the cationic nitrosyls with other nucleophiles was less successful. Although $NaBD_4$ gave the deuteriated analogues of the complexes (III), addition of methyllithium to diethyl ether suspensions of (II; L = $Me_6C_6$, $Me_5HC_5$, or 1,2,4,5-$Me_4H_2C_6$) resulted in only very low yields of cyclohexadienyls containing *exo*-methyl substituents. Such species could only be characterised by their i.r. spectra [*e.g.* for (III; L = *exo*-1,2,4,5,6-$Me_5H_2C_6$), $\bar{\nu}$(CO) = 2 005 and 1 947 and $\bar{\nu}$(NO) = 1 689 $cm^{-1}$] and by observation of parent ions and carbonyl and nitrosyl loss

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[5] N. G. Connelly and L. F. Dahl, *Chem. Comm.*, 1970, 880.

in the mass spectrum. Insufficient quantities for n.m.r. or analytical studies were obtained.

Addition of halide ions to solutions of the cations (II) again produced reactions which suggested cyclohexadienyl formation but no stable products were isolated. For example, in $CHCl_3$, $[Pr^i_4N][Cl]$ and (II; $n = 0$) afforded a deep orange-red solution which showed i.r. bands at 2 043, 1 957, and 1 692 $cm^{-1}$. The number of bands observed suggests that carbonyl displacement by halide ion does not occur, and the lowering in wavenumber from the values of the cation suggests formation of a chlorocyclohexadienyl has taken place. Unfortunately no stable product was isolated and thus confirmation of the existence of these chlorocyclohexadienyl complexes cannot be made.

*Spectral Studies*.—I.r. spectra of the cationic arene, (II), and neutral cyclohexadienyl complexes, (III), are recorded in Table 1. In the carbonyl and nitrosyl regions the band positions varied as expected with increased methyl substitution at the organic ring, causing reduction in wavenumber of both ν(CO) and ν(NO). However, in the case of complexes (III), only the substituents on the five carbon atoms involved in bonding to the metal atom influenced the position of the absorptions. Thus (III; L = *endo*-$Me_6HC_6$ and 1,2,3,4,5-$Me_5H_2C_6$) had virtually identical spectra. This observation allows partial identification of the minor isomers formed in the reactions of $NaBH_4$ with (II). Thus, the i.r. spectrum of the minor isomer formed from (II; L = 1,2,4,5-$Me_4H_2C_6$) showed absorption at 2 011, 1 956, and 1 694 $cm^{-1}$. The fact that these absorptions occurred at higher wavenumber than those of (III; L = 1,2,4,5-$Me_4H_3C_6$), the major product from the reaction, is good evidence that the additional product is (III; L = *endo*-1,3,4,6-$Me_4H_3C_6$). In a similar fashion, observation of bands at 2 005, 1 948, and 1 686 $cm^{-1}$ for the product of the reaction of methyl-lithium and (II; $n = 1$) is in good agreement with the suggested formation of (III; L = *exo*-$Me_6HC_6$). The expected [6,7] *exo*-attack of $H^-$ on the arene ring was confirmed by the observation of low-frequency C–H i.r. absorptions attributable to the *exo* C–H bond. For example (III; L = *endo*-$Me_6HC_6$ and 1,2,4,5-$Me_4H_3C_6$) showed strong peaks at 2 770 and 2 760 $cm^{-1}$ respectively in $CS_2$. No such peaks occurred for the deuteriated analogues.

The $^1H$ n.m.r. spectra of complexes (II) (Table 2) were similar to those of (I). Where non-equivalent methyl groups occurred, no attempt was made to assign each resonance. A full analysis of the spectra of (I) has been presented [8] and it is probable that similar assignments hold for the isoelectronic cations (II). $^1H$ N.m.r. spectra of complexes (III) (Table 3) were assigned using arguments similar to those used by Khand *et al.* in discussion of the spectra of (η-cyclohexadienyl)(η-cyclopentadienyl)iron complexes.[7] Thus, as a general observation, the methyl resonances observed at highest field are assignable to the methyl groups nearest to the CHR group of the cyclohexadienyl ring. The assignments of the spectra of (III) are self consistent and fit the general rules of Khand *et al.* after making allowance for the difference in solvent used for the spectral measurements [*i.e.* $^1H$ n.m.r. resonances for the 6-(*endo*), 1(5)-, 2(4)-, and 3-methyl groups occurred in the regions $\tau$ 8·8—8·9, 8·5—8·7, 8·1—8·3, and 7·4—7·6 respectively (in $CDCl_3$)].

In contrast to the observations of Khand *et al.*, the *endo*-methyl and *exo*-H resonances of the CHMe group of (III; L = *endo*-$Me_6HC_6$) were not coincident and each signal showed hyperfine splitting. The *exo*-H resonance was partially obscured by that of the 3-Me signal, but it was clearly a quartet with *J*(HH) 7 Hz. Similar coupling was found for the doublet assigned to the *endo*-Me signal. On deuteriation the quartet disappeared and the *endo*-Me doublet became a broad singlet. In the n.m.r. spectra of the penta- and tetra-methylcyclohexadienyls the resonance of the $CH_2$ group of the ring occurred as an irregular doublet at $\tau$ 8—8·1 and no coupling constants between *exo*- and *endo*-protons could be measured. In each case deuteriation led to broadening of the signals to ill defined singlets. The n.m.r. spectrum of (III; L = 1,2,3,4-$Me_4H_3C_6$) not only showed the irregular $CH_2$ doublet but also a doublet of doublets for $H_1$ due to coupling with *exo*-$H_6$ [*J*(HH) 2 Hz] and with *endo*-$H_6$ [*J*(HH) 5 Hz]. Deuteriation in this case caused the coupling between $H_1$ and *exo*-$H_6$ to be lost, confirming the assignment and also that *exo* $H^-$ or $D^-$ attack on (II; L = 1,2,3,4-$Me_4H_2C_6$) occurs.

## DISCUSSION

The cations (II) and the manganese analogues $[Mn(CO)_3L]^+$ undergo a series of reactions with nucleophiles. While (II) only afford cyclohexadienyls with $H^-$, $D^-$, and $Me^-$, the manganese cations have been shown to also react with $CN^-$,[9] $Ph^-$,[10] and with less-common nucleophiles such as $N_3^-$, $NCO^-$, and the diethyl malonate and pentane-2,4-dionate anions.[11] It is, however, not possible to assign these apparent differences in reactivity to any effect of the nitrosyl group. Although it would be tempting to suggest that the nitrosyl ligand deactivates the arene ring towards nucleophilic attack, there is, as yet, little evidence to support this. The i.r. spectra of the manganese [9] and chromium species in the carbonyl region show absorptions at very similar wavenumbers for a given arene suggesting very little difference in electron density at the metal atom. The n.m.r. spectra of the arene cations do show that the resonances of the arene protons occur at lower field in the chromium species, possibly indicative of higher electron density on the arene ligand and thus reduced ability to interact with nucleophiles. Such arguments would suggest that the $NO^+$ ligand must be either a poorer π-acceptor or better σ-donor than CO. The former suggestion, however, is certainly in disagreements with i.r. spectroscopic results on $[Co(CO)_3(NO)]$ and its derivatives.[12] It therefore appears that for this particular set of isoelectronic complexes, the effect of the nitrosyl ligand is slight. Further studies on other systems will show whether this is a general or unusual observation.

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## EXPERIMENTAL

The preparation and purification of the complexes described were carried out under an atmosphere of dinitrogen unless otherwise stated. Complexes $[Cr(CO)_3L]$ (I; L = arene) were prepared by the method of Nicholls and Whiting [13] and were recrystallised from di-isopropyl ether or, when L = $C_6Me_6$, from dichloromethane–hexane. $[NO][PF_6]$ Was purchased from Ozark Mahoning Co. Ltd., Tulsa, Oklahoma, and $NaBD_4$ from Stohler Isotope Chemicals, Montreal, Canada. All solvents were dried by standard methods and deoxygenated before use.

I.r. spectra were recorded on Perkin-Elmer PE257 or PE457 spectrophotometers using, in the case of solution spectra, the × 10 expansion facility on the former. N.m.r. spectra were recorded on Varian Associates HA100 or T60 instruments. Mass spectra were recorded on an A.E.I. MS9 spectrometer. Microanalyses were carried out by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol. M.p.s are uncorrected.

*Dicarbonyl(η-hexamethylbenzene)nitrosylchromium Hexafluorophosphate*, (II; *n* = 0).—*Method* (a). To (I; L = $C_6Me_6$) (0·45 g) in a mixture of toluene (30 cm$^3$) and methanol (6 cm$^3$) was added $[NO][PF_6]$ (0·35 g). After vigorously stirring for 10 min, a yellow solid was filtered off from the red solution. The *complex* was washed well with diethyl ether and air dried, yield 0·38 g (56%). The complex may be recrystallised from acetone–diethyl ether and is soluble in polar solvents such as acetone, $CH_2Cl_2$, or nitromethane to give yellow solutions which slowly decompose in air. The penta- and tetra-methylbenzene analogues were prepared by the same method; yields are given in Table 1.

*Method* (b). To a deep red solution of (I; L = $C_6Me_6$) (0·5 g) in liquid $SO_2$ (10 cm$^3$) was added $[NO][PF_6]$ (0·4 g). After stirring for 10 min at −20 °C the resulting brown solution was evaporated to dryness. Recrystallisation of the residue from acetone–diethyl ether afforded the *complex*, yield 0·46 g (62%).

*Dicarbonyl*(1—5-η-endo-*hexamethylcyclohexadienyl*)*nitrosylchromium*, (III; L = endo-$Me_6HC_6$).—To (II; *n* = 0) (450 mg) suspended in tetrahydrofuran (thf) (30 cm$^3$) was added $NaBH_4$ (80 mg). After stirring for 90 min, the resulting red solution was filtered and evaporated to dryness. Chromatography on an alumina–hexane column gave an orange band which was eluted with hexane to give an orange-red solution. Evaporation to low volume followed by cooling to −80 °C gave red crystals which were separated from the mother liquor and dried *in vacuo*, yield 61 mg [20% based on (II; *n* = 0)]. The pure complex may be stored, without deterioration, at −20 °C under an atmosphere of dinitrogen. Solutions of the pure complex in hexane decompose slowly in air. The other cyclohexadienyl complexes in Tables 1 and 3 were prepared in a similar manner from the appropriate cation (II) and $NaBH_4$ or $NaBD_4$.

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