Table II. Crystallographic Data for 9

compd	$C_{16}H_{20}O_2P_2Rh_2$
mol wt	512.12
space group	$P\bar{1}$
cell dimens	
a, Å	7.188 (6)
b, Å	7.725 (6)
c, Å	8.675 (3)
α, deg	102.34 (5)
β, deg	96.26 (5)
γ, deg	102.05 (6)
cell V, Å^3	454
molecules/unit cell	1
D_{calcd}, g/cm^3	1.88
linear abs coeff, cm^{-1}	19.6
radiatn	Mo Kα
cryst dimens, mm	0.4 × 0.9 × 1.0
scan width, deg	$0.8 + 0.2 \tan \theta$
decay of stds	<1%
reflctns measd	1632
2θ range, deg	2-46
reflctns obsd	1528
no. of parameters varied	100
goodness of fit	1.11
R	0.036
R_w	0.041

Table III. Final Fractional Atomic Coordinates for 9

atom	x/a	y/b	z/c
Rh	-0.04511 (6)	-0.12779 (6)	0.68580 (5)
C(1)	0.1436 (9)	-0.1639 (9)	0.8215 (8)
O	0.2683 (8)	-0.1863 (9)	0.9066 (7)
P	0.1055 (2)	0.1668 (2)	0.7359 (2)
C(2)	0.301 (1)	0.263 (1)	0.9029 (9)
C(3)	-0.054 (1)	0.320 (1)	0.772 (1)
C(4)	-0.2105 (8)	-0.2237 (8)	0.4292 (7)
C(5)	-0.2164 (9)	-0.3789 (8)	0.4947 (7)
C(6)	-0.3165 (9)	-0.359 (1)	0.6278 (8)
C(7)	-0.3770 (9)	-0.199 (1)	0.6444 (9)
C(8)	-0.3052 (9)	-0.1104 (9)	0.5295 (8)

temperature over a 12-h period. The red-brown solution was filtered through a Celite plug and the THF was removed. The brown residue was chromatographed on an alumina column with benzene to produce a red band. The benzene was removed, and an IR spectrum was obtained in toluene: ν_{CO} 2022, 1968, 1948, and 1920 cm^{-1}. Attempts to separate the mixture by column chromatography or by fractional crystallization were not successful. A satisfactory ^{1}H NMR spectrum of the product could not be obtained.

X-ray Crystal Structure Determination for 9. Crystals were mounted in thin-walled glass capillaries. Final lattice parameters as determined from the least-squares refinement of the angular settings for 25 carefully centered reflections ($2\theta > 36°$) are given in Table II. Data were collected by the θ-2θ scan technique as described previously.[22] A summary of data collections and structure solution parameters is also given in Table II. Calculations were carried out by using the SHELX system of computer programs.[23] Structure solution was accomplished by the location of the rhodium atoms on the Patterson map, followed by the calculation of a difference Fourier map. All non-hydrogen atoms were treated with anisotropic thermal parameters. Hydrogen atoms were not located. The final value of R equals 0.036 and R_w equals 0.041. The weighting scheme was based on unit weights. No unaccounted electron density was found on a difference Fourier map. Final values of the positional parameters are given in Table III.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research program (M.D.R.). We are also grateful to Prof. H. G. Alt for assistance in obtaining some of the mass spectra, to Johnson-Matthey, Inc., for a generous loan of rhodium trichloride, and to Dr. R. Poilblanc for information on his related studies prior to publication.

Supplementary Material Available: Tables of anisotropic thermal parameters and final fractional atomic coordinates for all atoms (2 pages); a listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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Dicarbonylnitrosyl(cyclohexadienyl)rhenium Cations: Synthesis, Electrochemistry, and Nucleophilic Addition Reactions

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Grignard reagent addition to [(arene)Re(CO)$_3$]PF$_6$ (**1b**) gives the corresponding (cyclohexadienyl)Re(CO)$_3$ complexes (**2b**). When the dienyl carbons in **2b** all bear methyl substituents, treatment with NOPF$_6$ affords the nitrosyl salts [(cyclohexadienyl)Re(CO)$_2$NO]PF$_6$ (**3b**). Hydride (NaBH$_4$) adds to the ring in **3b** to give (cyclohexadiene)Re(CO)$_2$NO (**4b**) in which the hydride is situated stereospecifically endo to the metal. Other nucleophiles (CN$^-$, CH(CO$_2$Me)$_2^-$, PBu$_3$) react with **3b** to substitute a CO ligand; this also occurs with the manganese analogues **3a** when the dienyl portion of the six-membered ring is permethylated. Reduction of [(cyclohexadienyl)M(CO)$_2$NO]PF$_6$ in dichloromethane at a platinum electrode occurs at nearly the same potential for both manganese and rhenium, with the important distinction that the latter is reduced in a chemically reversible manner while the former is completely irreversible. Steady-state voltammetry at platinum disk microelectrodes shows that the first reduction of [(1,2,3,4,5-pentamethyl-6-*exo*-phenylcyclohexadienyl)Re(CO)$_2$NO]PF$_6$ is quasi-reversible in dichloromethane at electrodes in the 1-10 μm diameter range; the standard heterogeneous charge-transfer rate constant is estimated as 0.1 cm/s.

Introduction

Coordination of cyclic π-hydrocarbons to transition metals offers the potential for ring functionalization via routes normally inaccessible in organic synthesis. Most commonly, coordination results in electrophilic activation; subsequent nucleophilic addition produces a monofunc-

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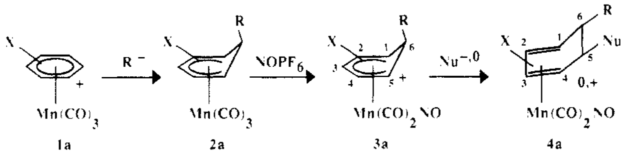
Scheme I



tionalized π-hydrocarbon. Thus, there are numerous examples of useful single nucleophilic additions to complexed arene and cyclohexadienyl rings.[1-3]

The addition of two nucleophiles to coordinated arenes is an attractive route to cis-difunctionalized cyclohexadienes. However, examples of this procedure are rare because the π-hydrocarbon activation is reduced or lost after the first nucleophile adds. Several examples of double addition to arenes have been reported,[4-7] but these have restricted utility because either one (or both) of the nucleophiles must be hydride or the nucleophiles that work are limited to a very few. The difunctionalization of the arene in (arene)$Cr(CO)_3$ by a nucleophile addition–electrophile addition sequence is known[8,9] to be possible but suffers from the requirement that the nucleophile be a very strong one. Double nucleophile addition to a benzene in $(C_6H_6)_2Fe^{2+}$ has been realized[10] by the four-step reaction sequence of hydride addition, $PhCH_2MgBr$ addition, low-temperature hydride extraction with Ph_3C^+, and finally attack by KCN. The possible extension of this procedure to a variety of carbon nucleophiles will depend on the stability of the 17-electron radicals that are produced during the "hydride" abstraction step. The synthesis of difunctionalized cyclohexadienes via the intermediacy of (cyclohexadienyl)$Fe(CO)_3^+$ is also known[11,12] but is limited by the difficulty of preparing such complexes with the required non-hydrogen substituent on the saturated carbon in the cyclohexadienyl ring.

We recently found a procedure that, with suitable modifications, appears to be a general one for the synthesis of coordinated cis-difunctionalized cyclohexadienes.[13] The chemistry is summarized in Scheme I. The first nucleophile (R^-) can be one of a variety of carbon or hydride donors.[14] Following reactivation of **2a** by conversion to **3a**, a second nucleophile ($Nu^{-,0}$) can be added to effect the arene difunctionalization. The reaction **3a** → **4a** proceeds smoothly with hydride, phosphorus, and nitrogen donors, but carbon donors are plagued by what is apparently single electron-transfer processes. Fortunately, these unwanted redox steps can be largely eliminated by replacing one or two of the CO ligands in **3a** by tertiary phosphine ligands (e.g., PBu_3 or diphos).[15] Similar chemistry obtains[16] when a phosphine ligand is substituted for CO in (cycloheptadienyl)$Mn(CO)_2NO^+$, the seven-membered analogue of **3a**.

With a hydride donor as the nucleophile, the reaction **3a** → **4a** is quite unusual in that the hydride adds stereospecifically endo to the metal instead of the normal exo position.[13] This is also true if the $Mn(CO)_2NO$ moiety in **3a** is replaced by $Mn(CO)(PR_3)NO$ or if the cyclohexadienyl ring is replaced by a cycloheptadienyl ring. The only other reported example of stereospecific endo hydride addition to a coordinated ring deals with [(thiabenzene 1-oxide)$Cr(CO)_2NO]PF_6$, which reacts to give a σ,π-allyl product.[17]

The goal of the present work was to investigate the chemistry in Scheme I with manganese replaced by rhenium (complexes **1b**–**4b**). It was thought that the hitherto unknown rhenium complexes **3b**, if they can be synthesized, may show interesting and useful differences compared to the manganese analogues. Of special interest are (1) the electrochemical behavior of **3b**, (2) the reactivity of **3b** with nucleophiles, and (3) the stereochemistry of hydride addition to **3b**.

The starting point for the rhenium-based chemistry is (arene)$Re(CO)_3^+$ (**1b**). Early attempts[18] to synthesize **1b** salts gave low yields due to the rapid solvolysis of (arene)$Re(CO)_3^+$ in oxygen donor solvents. More recent studies indicate how to avoid this difficulty.[19,20] Kinetic studies[19,21] of PBu_3 addition to the arene in **1a** and **1b** show that the arene ring is electrophilically activated to almost exactly the same degree for both metals, suggesting that the generalized conversions **1a** → **2a** and **1b** → **2b** may have similar chemical characteristics for the two metals. Nucleophilic addition to the arene in **1b** to give **2b** has been reported for the nucleophiles BH_4^-, AlH_4^-, CN^-, and PBu_3.[18-20] The addition of Grignard reagents is reported in this paper. Although **1b** readily suffers arene ring displacement by oxygen donors, the cyclohexadienyl complexes **2b** are more stable, roughly comparable to the manganese analogues.

We show in this paper that the rhenium nitrosyl salts **3b** can indeed be made from **2b** and that they react with nucleophiles to give either ring addition or CO substitution. As with manganese, it is shown that hydride adds to the ring in **3b** in a stereospecific endo manner, probably via a metal formyl intermediate.

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Table I. Spectral Data for [(Cyclohexadienyl)M(CO)$_2$NO]PF$_6$ Complexes (M = Mn, Re)[a]

M	X	R	yield,[b] %	ν_{CO}[c]	ν_{NO}[c]	^{1}H NMR δ (J, Hz)
Re	1,2,3,4,5-Me	Ph[d]	17[e]	2090, 2043	1795	7.10 (Ph), 4.27 (s, H^6), 3.00 (s, Me^3), 2.55 (s, Me^{2,4}), 2.33 (s, Me^{1,5})[f]
Re	1,2,3,4,5-Me	Me[g]	62[h]	2088, 2041	1791	3.09 (q, J = 6.5, H^6), 2.97 (s, Me^3), 2.51 (s, Me^{2,4}), 2.27 (s, Me^{1,5}), 0.74 (d, J = 6.5, Me^6)[f]
Re	1,2,3,4,5,6-Me	Me	52[i]	2088, 2040	1793	2.96 (s, Me^3), 2.55 (s, Me^{2,4}), 2.11 (s, Me^{1,5}), 1.38 (s, Me$^{6\text{-endo}}$), 0.74 (s, Me$^{6\text{-exo}}$)[f]
Mn	1,2,3,4,5-Me	Ph	44	2090, 2054	1817	7.10 (Ph), 3.86 (s, H^6), 2.77 (s, Me^3), 2.22 (s, Me^{2,4}), 1.97 (s, Me^{1,5})[j]
Mn	1,2,3,4,5-Me	Me	76	2088, 2052	1814	2.79 (q, J = 6.5, H^6), 2.72 (s, Me^3), 2.21 (s, Me^{2,4}), 2.01 (s, Me^{1,5}), 0.74 (d, J = 6.3, Me^6)[f]
Mn	1,2,4,5-Me[k]	Ph	89	2094, 2056	1824	7.15 (Ph), 6.69 (s, H^3), 4.26 (s, H^6), 2.26 (s, Me^{2,4}), 2.00 (s, Me^{1,5})[l]

[a] See Scheme I for numbering (**3a**,**b**). [b] Yield from tricarbonyl (**2a**,**b**). [c] cm^{-1} in CH$_2$Cl$_2$. [d] FAB-MS parent peak *m/e* 498. [e] Anal. Calcd (Found): C, 35.5 (34.5); H, 3.2 (3.2); N, 2.2 (2.1). [f] In CD$_2$Cl$_2$. [g] FAB-MS parent peak *m/e* 436. [h] Anal. Calcd (Found): C, 28.9 (27.8); H, 3.3 (3.1); N, 2.4 (2.2). [i] Anal. Calcd (Found): C, 30.3 (30.2); H, 3.6 (3.3); N, 2.4 (2.3). [j] In CDCl$_3$. [k] From ref 13. [l] In CD$_3$NO$_2$.

As mentioned above, single electron transfer often occurs when carbanions are reacted with the manganese cations **3a**. In fact, redox chemistry is a common problem with many intended nucleophilic additions to organometallic electrophiles. With respect to manganese and rhenium chemistry, voltammetric studies in our laboratory show[22] that CpMn(CO)$_2$NO$^+$ and **3a** give chemically irreversible reductions at ordinary sweep rates (ca. 1 V/s). However, CpMn(diphos)NO$^+$, (cyclohexadienyl)Mn(diphos)NO$^+$, and CpRe(CO)$_2$NO$^+$ are reduced in a chemically reversible manner. Thus, there was reason to suspect that **3b** may be reversibly reduced, and noting that diphos substitution for the CO's in **3a** decreases the role of single electron transfer in nucleophilic additions, there was also reason to suspect that the reactions of **3b** would not be prone to redox pathways.

In addition to electrochemical experiments with conventional platinum disk electrodes (diameter ≥ 1 mm), we report herein voltammetric studies of **3b** and related complexes utilizing microelectrodes (diameter ≤ 25 μm).[23] A particularly attractive feature of microelectrodes is the ready accessibility of a steady-state current response at low sweep rates (ca. 20 mV/s), which is due to the predominance of radial (convergent) diffusion under these conditions.[23,24] The effective time domain of steady-state experiments can be readily adjusted by varying the size of the electrode, which for platinum disks are easily fabricated with a diameter as small as 1 μm.[25] This permits the determination of very rapid heterogeneous charge transfer rate constants (k_s). Recent theoretical advances show how to extract the k_s values for charge transfer that is irreversible, quasi-reversible, or nearly reversible at inlaid disk electrodes.[26,27] Using steady-state cyclic voltammetry, we present herein an analysis of charge transfer from platinum disk microelectrodes to the new rhenium complexes.

Experimental Section

General Data. All solvents were purified by standard methods and all synthetic procedures were carried out under an atmosphere of nitrogen or argon. IR spectra were recorded on a Mattson Alpha Centauri FTIR, and ^{1}H NMR spectra were obtained on a Bruker WM250 or AM400 instrument. [(Cyclohexadienyl)Mn(CO)$_2$NO]PF$_6$ complexes (**3a**) were synthesized as previously described.[13] Spectroscopic data for these compounds are given in Table I.

[(Arene)Re(CO)$_3$]PF$_6$ (1b). In previous work these complexes were synthesized by reacting Re(CO)$_5$Br and AlCl$_3$ with the arene at moderate temperatures.[19] More consistent and generally better yields are realized by the use of higher temperatures. For example, a mixture of Re(CO)$_5$Br (1.6 g, 4.0 mmol), freshly sublimed AlCl$_3$ (1.6 g, 12 mmol), and pentamethylbenzene (3.0 g, 20 mmol) were combined in 10 mL of decane and heated to 150 °C for 1 h. The product formed as a red solid beneath the clear decane. After the solution was cooled in an ice bath, the decane was decanted and the red solid was washed twice with cyclohexane and then dissolved in 20 mL of ice water. As soon as a homogeneous solution was achieved, the water was filtered through a coarse sintered glass frit into a solution of NH$_4$PF$_6$ (0.73 g, 4.5 mmol in 5 mL of water). The white precipitate of [(C$_6$HMe$_5$)Re(CO)$_3$]PF$_6$ was filtered and recrystallized by dissolving in acetone and immediately precipitating by the addition of diethyl ether. The yield was 71% (1.6 g, 2.9 mmol). The hexamethylbenzene complex **1b** was prepared similarly.

With less methylated arenes an alternative method for synthesizing **1b** was employed that follows the procedure of Calderazzo et al.[20] and avoids the aqueous extraction step (vide supra). For example, for the benzene complex, Re(CO)$_2$Br and AlCl$_3$ were refluxed in neat benzene for 4 days. The solvent was decanted off and CH$_2$Cl$_2$ added to give a red solution that was filtered under argon. The resulting solution of [(C$_6$H$_6$)Re(CO)$_3$]AlCl$_3$Br could be stored for several weeks at −10 °C. The complex was not isolated, and Grignard reagents were added directly to the red solution at low temperature to produce the neutral complex **2b** (vide infra).

[(Cyclohexadienyl)Re(CO)$_3$] (2b). The Grignard reagents MeMgCl and PhMgBr were successfully added to **1b** (arene = benzene, mesitylene, pentamethylbenzene, hexamethylbenzene) to give the neutral cyclohexadienyl complexes **2b**. The following is a typical synthesis starting with any of the **1b** complexes except [(benzene)Re(CO)$_3$]PF$_6$. To a solution of [(C$_6$HMe$_5$)Re(CO)$_3$]PF$_6$ (0.45 g, 0.80 mmol) in 20 mL of CH$_2$Cl$_2$ at 0 °C was added a diethyl ether solution of PhMgBr (3 mL, 3.0 M). The reaction mixture became yellow after stirring for 2 h. With the reaction flask in an ice bath, 1 mL of ice water was added to destroy excess Grignard reagent. The reaction mixture was extracted with 50 mL of diethyl ether and dried over MgSO$_4$. Solvent evaporation left a somewhat air-sensitive brown oil that was chromatographed on a neutral alumina column with 1:1 hexane–diethyl ether to yield 0.28 g (70% yield) of a colorless oil. IR (ν_{CO}, CH$_2$Cl$_2$): 2008, 1915 cm^{-1}. All **2b** complexes synthesized with PhMgBr or MeMgCl are colorless to light yellow oils or solids. They have two strong ν_{CO} IR bands in the range 2015–2004 and 1926–1912 cm^{-1}, with the frequencies decreasing with increasing arene ring methylation; the lower frequency ν_{CO} band is broad and at high resolution can be resolved into two overlapping bands.

Grignard reagent addition to **1b** (arene = benzene) was effected as follows. A tenfold excess of PhMgBr in diethyl ether was added to a CH$_2$Cl$_2$ solution of [(C$_6$H$_6$)Re(CO)$_3$]AlCl$_3$Br (vide supra) at −78 °C. The initial red solution rapidly turned yellow-orange. The reaction mixture was warmed to room temperature and treated with ice water. The organic layer was diluted with diethyl ether and dried over Na$_2$SO$_4$. Solvent evaporation left a yellow oil that was dried in vacuo. IR (ν_{CO}, CH$_2$Cl$_2$): 2023, 1932 cm^{-1}. IR (ν_{CO}, C$_5$H$_{12}$): 2030, 1950, 1940 cm^{-1}. The corresponding methyl analogue (C$_6$H$_6$Me)Re(CO)$_3$ was prepared similarly and has IR bands in CH$_2$Cl$_2$ at 2021 and 1928 cm^{-1}. The **2b** complexes[28] were

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Table II. Spectral Data for (Cyclohexadiene)$M(CO)_2NO$ Complexes (M = Mn, Re)[a]

M	X	R	ν_{CO}	ν_{NO}	^1H NMR δ (J, Hz)
Re	1,2,3,4,5-Me	Ph[b]	2023, 1967[c]	1707[c]	7.00 (Ph), 3.66 (d, J = 11.5, H^6), 2.73 (dq, J = 11.4, 7.2, H^5), 2.61 (s, Me^2), 2.60 (s, Me^3), 1.84 (s, Me^1), 1.53 (s, Me^4), 0.39 (d, J = 7.2, Me^5)[e]
Re	1,2,3,4,5-Me	Me	2023, 1966[c]	1706[c]	2.53 (s, $Me^{2,3}$), 1.84 (s, $Me^{1,4}$), 0.81 (d, J = 6.8, $Me^{5,6}$)[f]
Mn	1,2,3,4,5-Me	Me	2021, 1969[c]	1734[c]	2.34 (m, $Me^{5,6}$), 2.17 (s, $Me^{2,3}$), 1.65 (s, $Me^{1,4}$), 0.81 (d, J = 6.8, $Me^{5,6}$)[f]
Mn	1,2,4,5-Me[g]	Ph	2024, 1972[d]	1737[d]	6.99 (Ph), 5.38 (s, H^3), 3.64 (d, J = 11, H^6), 2.48 (dq, J = 11, 7 H^5), 2.20 (s, Me^2), 1.60 (s, Me^1), 1.41 (d, J = 7, Me^4), 0.41 (d, J = 7, Me^5)[e]

[a] See Scheme I for numbering (**4a,b**). [b] FAB-MS, m/z 500 (M^+ + 1), 469 (M^+ − NO or M^+ − 2 Me), 454 (M^+ − NO − Me or M^+ − 3 Me), 439 (M^+ − NO − CO or M^+ − NO − 2 Me), 426 (M^+ − NO − 3 Me or M^+ − 5 Me), 408 (M^+ − NO − 2 CO or M^+ − NO − 4 Me), 394 (M^+ − NO − 5 Me). [c] cm^{-1} in pentane. [d] cm^{-1} in hexane. [e] In $CDCl_3$. [f] In CD_2Cl_2. [g] From ref 13.

generally converted immediately after synthesis to the nitrosyl salts **3b**.

[(Cyclohexadienyl)$Re(CO)_2NO]PF_6$ (3b). In a typical synthesis, $(C_6Me_7)Re(CO)_3$ (0.065 g, 0.145 mmol) was dissolved in 10 mL of CH_2Cl_2 and 1 mL of $MeNO_2$ under argon. While the solution was stirred at room temperature, $NOPF_6$ (0.028 g, 0.16 mmol) was added. After 30 min the solution was filtered and concentrated to 5 mL and diethyl ether slowly added to precipitate $[(C_6Me_7)Re(CO)_2NO]PF_6$ as orange crystals in a 52% yield (0.045 g, 0.075 mmol). Crystals suitable for X-ray diffraction studies may be obtained by adding diethyl ether to a MeCN solution and cooling to −10 °C. The other **3b** complexes successfully synthesized were $[(C_6HMe_6)Re(CO)_2NO]PF_6$ (62%) and $[(C_6HMe_5Ph)Re(CO)_2NO]PF_6$ (17%). Table I gives spectral data for these complexes as well as for several manganese analogues, which were synthesized as previously described.[13] The (cyclohexadienyl)$Re(CO)_3$ complexes derived from **1b** with arene = benzene and mesitylene could not be converted to the nitrosyl salts **3b** (vide infra).

Hydride Addition to [(Cyclohexadienyl)$M(CO)_2NO]PF_6$ (3a,b). The general procedure was to dissolve **3a** or **3b** in 2:1 MeCN/THF at −5 °C. Excess $NaBH_4$ was added and the mixture stirred for 1 h. The solvent was evaporated with a stream of nitrogen and the residue extracted into pentane and chromatographed on neutral alumina to give a moderately air-stable orange oil. The yields were quantitative as judged by IR spectroscopy; isolated yields were ca. 65%. Table II gives spectroscopic data for the (cyclohexadiene)$M(CO)_2NO$ complexes (**4a,b**) synthesized by this method.

Addition of Other Nucleophiles to [(Cyclohexadienyl)M-$(CO)_2NO]PF_6$ (3a,b). Several reactions were carried out at room temperature on a small scale and monitored by IR spectroscopy. The experiments were limited to **3a** and **3b** containing 6-*exo*-methyl- and 6-*exo*-phenyl-1,2,3,4,5-pentamethylcyclohexadienyl rings. Cyanide was added as Ph_4AsCN or Et_4NCN in CH_2Cl_2 to a solution of **3a** or **3b** in CH_2Cl_2. With the rhenium complexes the color changed rapidly (ca. 1 s) from yellow to orange to yellow. IR spectra taken within 1 min of mixing for cyanide addition to **3a** and **3b** indicate that ring addition did not occur but rather CO substitution by CN^- took place; for example, the product with **3b** (6-*exo*-phenyl) had ν_{CO} = 2001 and ν_{NO} = 1729 cm^{-1} in CH_2Cl_2. Similarly, the nucleophiles PBu_3 and $CH(CO_2Me)_2^-$ reacted by substituting for a CO ligand. IR experiments at −70 °C in CH_2Cl_2 showed that Et_4NCN and PBu_3 react with **3b** to give CO displacement with no spectral evidence for intermediate species arising from intial attack on the ring.

Electrochemistry. All electrochemical experiments were done under a blanket of argon or nitrogen in CH_2Cl_2 with 0.10 M Bu_4NPF_6 ($TBAPF_6$). Conventional cyclic voltammetry was done with EG&G 173 or BAS CV27 potentiostats in a three-electrode configuration. The voltage ramp was either generated internally or fed in from an EG&G 175 programmer. The working electrode was a platinum disk (diameter 1.6 mm), a glassy carbon disk (diameter 3.0 mm), or a hanging mercury drop, and the counter electrode was a platinum wire. The reference was a Metrohm Ag/AgCl electrode filled with CH_2Cl_2/0.1 M $TBAPF_6$ and saturated with LiCl; this was separated from the test solution by a salt bridge containing CH_2Cl_2/0.1 M $TBAPF_6$. Bulk electrolysis was done with an EG&G 173 potentiostat and a 170 digital coulometer. The working electrode was a mercury pool, the counter electrode was a platinum mesh, and the reference electrode was Ag/AgCl (vide supra).

Steady-state voltammetry with platinum disk microelectrodes utilized a two-electrode configuration with a Ag/AgCl reference. The electrochemical cell was placed inside a solid aluminum Faraday cage. An EG&G 175 programmer provided the voltage ramp and a Keithley Model 427 current amplifier was used to convert current to a voltage signal that was stored on floppy disks via a Nicolet NIC-310 digital oscilloscope. Hard copies were displayed on a X-Y recorder or an IBM digital plotter. The platinum disk microelectrodes of radius 12.5 to 0.5 μm were fabricated in this laboratory as previously described.[25]

IR spectroelectrochemistry was performed with an optically transparent thin-layer cell which was constructed on the basis of a design by Mann et al.[29] Between NaCl or CaF_2 windows in a SPECAC demountable cell were placed two 1000 gauge Tefzel gaskets (a gift of E. I. du Pont de Nemours and Co.). A gold mesh electrode (500 lines/in., Buckbee-Mears Co.) was placed between the gaskets. The gaskets were heat sealed at their protrusion along the edges of the salt windows. A small platinum wire immersed in the upper filling port served as a pseudo reference electrode. The body of the cell itself was used as the counter electrode. Samples were prepared at 1.0 mM concentration in CH_2Cl_2/0.2 M $TBAPF_6$. The solution was loaded into the cell under argon, and the applied potential was provided by an EG&G 173 potentiostat.

Results and Discussion

Synthesis of Rhenium Complexes. The (arene)Re-$(CO)_3^+$ complexes **1b** are not particularly difficult to synthesize but are subject to rapid arene ring displacement by oxygen donor solvents. The more methylated species, e.g., arene = C_6Me_6 and C_6HMe_5, are much more stable in this regard, probably due to a stronger Re–arene bond and steric hindrance to solvent attack at the metal. In comparison, the manganese analogues are much more stable to arene displacement.

The addition of Grignard reagents to the arene in **1a** and **1b** occurs readily to give **2a** and **2b**. The ^1H NMR spectra of **2a** and of the nitrosyl salts derived from these (**3a**, Table I) show conclusively that, as expected, the Grignard reagent adds exo to an unsubstituted carbon on the arene.[13,14] It was previously shown[30] that nucleophiles add to the ring in **1b** in an exo manner; this is consistent with our NMR data.[28] For **1a**, but not **1b**, there was evidence of some steric hindrance created by the ring methyls.

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(28) ^1H NMR data for **2b** (X = H, R = Ph): δ 7.0–7.5 (Ph), 5.79 (tt, J = 5.2, 1.4 Hz, H^3), 5.20 (ddd, J = 7.4, 5.3, 0.8 Hz, $H^{2,4}$), 4.09 (t, J = 5.6 Hz, H^6), 3.87 (ddd, J = 7.2, 5.9, 1.3 Hz, $H^{1,5}$). X = H, R = Me: δ 5.80 (tt, J = 5.1, 1.5 Hz, H^3), 4.99 (ddd, J = 7.3, 6.1, 1.0 Hz, $H^{2,4}$), 3.58 (ddd, J = 7.2, 5.7, 1.4 Hz, $H^{1,5}$), 2.83 (sextet t, J = 6.3, 1.0 Hz, H^6), 0.52 (d, J = 6.5 Hz, Me^6). X = 1,2,3,4,5-Me, R = Me: δ 2.83 (q, J = 6.4 Hz, H^6), 2.51 (s, Me^3), 2.27 (s, $Me^{2,4}$), 1.90 (s, $Me^{1,5}$), 0.46 (d, J = 6.4 Hz, Me^6).

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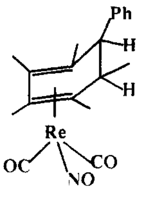
Thus, PhMgBr addition to $[(C_6HMe_5)Mn(CO)_3]PF_6$ yielded as a byproduct the acyl complex $(C_6HMe_5)Mn(CO)_2(COPh)$. It was previously reported[31] that alkyllithiums react with **1a** by addition to a CO ligand as well as the arene, with the relative amount of the former increasing with the extent of arene methylation.

The conversion of **2a** to **3a** by treatment with $NOPF_6$ works smoothly regardless of the number of substituents on the ring (Table I and ref 13). The behavior of the rhenium complexes is very different in that the success of the nitrosylation step is dependent on the number of methyl groups on the cyclohexadienyl moiety in **2b**. While **3b** could be synthesized for the pentamethyl and hexamethyl systems, it could not be made from $(C_6H_3Me_3Ph)Re(CO)_3$. This complex also failed to convert to **3b** when treated with NO_2BF_4 or any of several other sources of NO^+ that were previously shown[32] to be successful in other types of nitrosylation reactions.

Reaction of $[(Cyclohexadienyl)M(CO)_2NO]PF_6$ with Nucleophiles. The addition of hydride donors to the ring in the manganese complexes **3a** is particularly interesting because it has been demonstrated by ^1H NMR, ^2H NMR, and X-ray diffraction studies[13,16] that the addition occurs stereospecifically endo to the metal. In contrast to this, NMR and X-ray studies indicate that non-hydride donors that add to the ring do so in an exo fashion.[13] The stereochemistry of hydride addition to the rhenium complexes **3b** was easy to ascertain by examining the ^1H NMR spectrum of the product of the reaction of $NaBH_4$ and $[(1,2,3,4,5\text{-pentamethyl-6-}exo\text{-phenylcyclohexadienyl})Re(CO)_2NO]PF_6$. Structures **5** and **6** illustrate the endo and exo products, respectively. On the basis of X-ray structures of $(cyclohexadiene)Mn(CO)_2NO$ complexes,[13] it is known that the H-5,H-6 dihedral angle in **5** is only a few degrees while in **6** it is near 90°. Hence, one expects the vicinal H-5,H-6 coupling constant to be large (ca. 10 Hz) in **5** and very small in **6**. As Table II shows, the coupling constant is 11.5 Hz, which is almost identical with that found in a number of manganese complexes analogous to **5**. This confirms that the product obtained in the present study was the endo complex **5** and not **6**.



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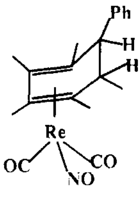

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Having established that hydride adds endo with both the manganese and rhenium complexes, the interesting question is why these complexes are so unusual in view of the fact that nucleophiles (including hydride) almost always add exo to coordinated cyclic π-hydrocarbons.[1] The endo hydride addition to **3a** and **3b** suggests an initial interaction with the metal or a CO ligand followed by migration to the ring. Since hydride addition to $(arene)Mn(CO)_3^+$ occurs exo for both manganese[33,34] and rhenium[30] and since the only example of stereospecific endo hydride addition other than with **3a** and **3b** contains the $Cr(CO)_2NO$ moiety,[17] one suspects that the nitrosyl ligand is necessary and may act as an electron sink if a metal hydride is formed as an intermediate. This, however, is not supported by the observation[35,36] of exo hydride addition to $(arene)Cr(CO)_2NO^+$. Preliminary low-temperature NMR experiments from our laboratory do not indicate a metal hydride intermediate but do, in the case of rhenium (**3b**), suggest the formation of a metal formyl species.[37] It is also possible that the initial interaction of **3a** and **3b** with hydride sources is single electron transfer to generate a 19- or 17-electron species depending on the bonding mode of the nitrosyl ligand. However, single electron transfer does not necessarily lead to an endo product, as shown by hydride addition to $CpFe(arene)^+$ complexes, which are known to involve initial electron transfer[38] but give the exo products.[36] Low-temperature IR and spectroelectrochemical (IR) studies underway should help to clarify the endo hydride addition mechanism.[37]

Unfortunately, IR spectra showed that nucleophiles other than hydride do not add to the ring in **3a** and **3b** complexes that have a methyl substituent at each unsaturated dienyl carbon. The nucleophiles include CN^-, $CH(CO_2Me)_2^-$, and PBu_3, and in each case clean CO substitution occurred. With the manganese complexes **3a** that have at least one unsubstituted dienyl carbon atom, nucleophiles generally add to the ring to give the cyclohexadiene product **4a**, although in some cases CO substitution can still occur.[13] As noted above, the rhenium cations **3b** could only be synthesized with heavily methylated dienyl rings, and, therefore, it would appear that generalized nucleophilic addition to $(cyclohexadienyl)Re(CO)_2NO^+$ to give coordinated dienes will not prove to be a useful reaction.

One obvious explanation for the above observations is that the methyl substituents present steric hindrance to nucleophilic attack (other than hydride) at the dienyl ring in permethylated **3a** and **3b**. There is precedent for such behavior, for example, in the reactions of $(C_6Me_6)Mn(CO)_3^+$ and $CpFe(C_6Me_6)^+$, which suffer nucleophilic attack at the CO or Cp ligands rather than the arene.[30,39] However, this does not mean that attack at the ring does not occur prior to final product formation. For example, we previously found[19] that PBu_3 adds to the ring in $(benzene)Mn(CO)_3^+$, which is then easily converted to $(benzene)Mn(CO)_2PBu_3^+$. Similarly, Mawby[40] found that cyanide addition to $(arene)Mn(CO)_3^+$ in polar media gives $(cyanocyclohexadienyl)Mn(CO)_3$ complexes that can be converted to $(arene)Mn(CO)_2CN$ products upon heating. An apparent exception to this is $(C_6Me_6)Mn(CO)_3^+$, which was reported[40] to react with cyanide in aqueous solution to give only CO substitution; however, we found[41] that, even for this permethylated system, Ph_4AsCN in CH_2Cl_2 adds cleanly and rapidly to the C_6Me_6 ring. Regarding the complexes of interest in this paper, we noted above that cyanide reactions with **3b** go through a rapid two-stage color change on the way to $(cyclohexadienyl)Re(CO)(CN)NO$. However, we were unable to find spectral evi-

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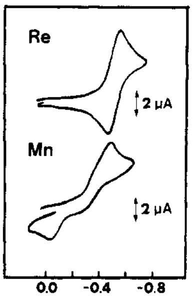

Figure 1. Cyclic voltammograms of 5.1 × 10^{-4} M [(1,2,3,4,5-pentamentyl-6-*exo*-phenylcyclohexadienyl)M(CO)$_2$NO]PF$_6$ (M = Re, Mn) at 0.20 V/s in dichloromethane at 20 °C. The working electrode was a 1.6-mm platinum disk, and the supporting electrolyte was 0.10 M TBAPF$_6$. The potential scale is adjusted so that the $E_{1/2}$ for ferrocene is equal to 0.45 V.

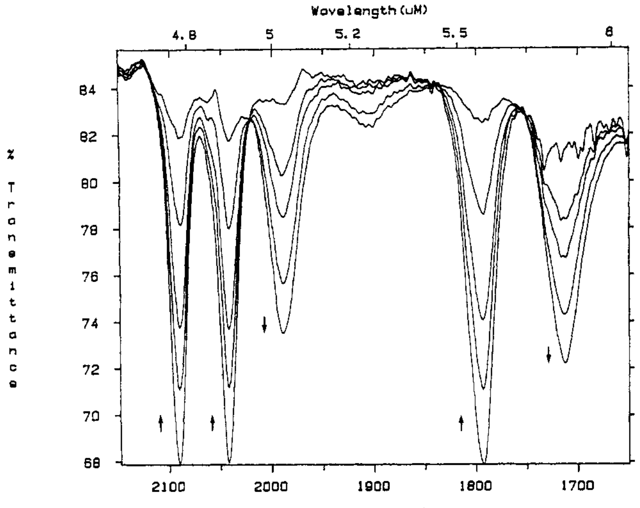

Figure 2. IR spectral changes for the reduction of 1.0 × 10^{-3} M [(1,2,3,4,5-pentamethyl-6-*exo*-phenylcyclohexadienyl)Re(CO)$_2$NO]PF$_6$ in a thin layer cell at 20 °C. The solvent was dichloromethane, and the electrolyte was 0.20 M TBAPF$_6$. The spectral scans shown correspond to a total electrolysis time of about 30 min.

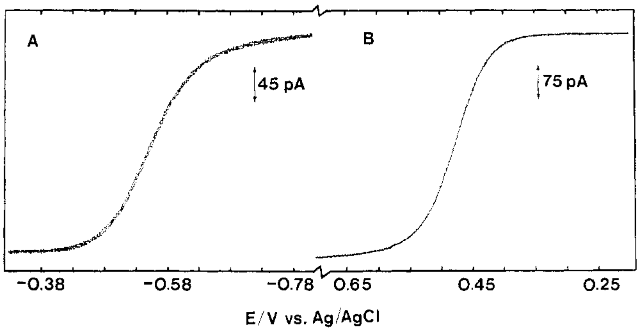

Figure 3. Steady-state cyclic voltammograms of (A) 0.6 × 10^{-3} M [(1,2,3,4,5-pentamethyl-6-*exo*-phenylcyclohexadienyl)Re(CO)$_2$NO]PF$_6$ and (B) 0.6 × 10^{-3} M ferrocene in dichloromethane at 20 °C with 0.10 M TBAPF$_6$. The working electrode was a 2-μm diameter platinum disk and the scan rate was 20 mV/s.

dence for an intermediate; even at −70 °C in CH$_2$Cl$_2$, IR spectra show only product and reactant during the course of the reaction (several minutes).

Electrochemistry. Cyclic voltammograms of [(1,2,3,4,5-pentamethyl-6-*exo*-phenylcyclohexadienyl)M(CO)$_2$NO]PF$_6$ (**7a**, M = Mn; **7b**, M = Re) at a conventional platinum electrode are illustrated in Figure 1. Similar results were obtained for all **3a** and **3b** complexes reported in this study. As Figure 1 shows, the manganese and rhenium complexes are reduced at similar potentials, which is consistent with our belief[21] that the ability to electrophilically activate coordinated π-hydrocarbons is about the same for both metals. It was also observed that **3a** and **3b** have a second (chemically irreversible) reduction at ca. 0.7–1.0 V negative of the first reduction. The most striking difference between the two metals is the chemically reversible nature of the first reduction with rhenium ($i_{p,a}/i_{p,c}$ = 1.0) and the chemically irreversible behavior with manganese. Indeed, reduction of **7a** remained chemically irreversible even at −90 °C, showing that the manganese radicals are far more reactive than the rhenium ones.

Bulk electrolysis of the rhenium complex **7b** in CH$_2$Cl$_2$ established that the first reduction involves 1.0 ± 0.1 electron. The results of a spectroelectrochemical experiment with **7b** in CH$_2$Cl$_2$ is shown in Figure 2. While some decomposition of the resulting radical to species not containing CO or NO probably occurred, Figure 2 suggests that reduction leads to loss of one CO, perhaps followed by dimerization.

Figure 3 gives the steady-state cyclic voltammogram of **7b** at a 2-μm diameter platinum disk electrode. The interesting feature here is the value of $|E_{1/4} - E_{3/4}|$, which is 78 mV for the rhenium complex and 59 mV for ferrocene. The ferrocene was placed in the same solution as the rhenium complex so that the experimental conditions were exactly the same for both voltammograms. For an electrochemically reversible process $|E_{1/4} - E_{3/4}|$ whould be 57 mV,[26] and we may conclude that within experimental error (±2 mV) ferrocene oxidation is nernstian at a 2-μm diameter platinum electrode, in agreement with previous observations.[42,43] The 78-mV value of $|E_{1/4} - E_{3/4}|$ for **7b** seen in Figure 3A means that the reduction is electrochemically quasi-reversible. By utilizing available theory[24,26,27] for steady-state voltammetry at microdisk electrodes, we estimate k_s to be 0.1 cm/s, which means that the reduction should appear reversible at conventional electrodes (after correcting for *iR* drop), in agreement with our observations. Interestingly, the analogous complex [CpRe(CO)$_2$NO]PF$_6$ undergoes much faster charge transfer and is fully reversible at a 1-μm diameter microelectrode.[22]

Summary. (Cyclohexadienyl)Re(CO)$_2$NO$^+$ (**3b**) complexes were synthesized in order to make comparisons to the previously reported manganese analogues **3a**. Whereas the manganese complexes are fairly easily synthesized, the rhenium cations can be made only with heavily alkylated cyclohexadienyl rings. Both **3a** and **3b** react with hydride donors to give (cyclohexadiene)M(CO)$_2$NO products in which the hydride is in an endo position. As expected, the reduction of **3** occurs at almost the same potential for both metals, although the resultant neutral radicals are much more chemically stable with the rhenium systems.

Acknowledgment. This work was supported by the National Science Foundation (Grant Nos. CHE-8521189 and CHE-8821588).

Registry No. **1b** (X = 1,2,3,4,5,6-H), 68927-90-2; **1b** (X = 1,3,5-Me), 84222-13-9; **1b** (X = 1,2,3,4,5-Me), 122648-13-9; **1b** (X = 1,2,3,4,5,6-Me), 100858-08-0; **2a** (X = 1,2,3,4,5-Me, R = Ph), 122648-29-7; **2a** (X = 1,2,3,4,5-Me, R = Me), 65700-53-0; **2a** (X = 1,2,4,5-Me, R = Ph), 95344-56-2; **2b** (X = 1,2,3,4,5-Me, R = Ph), 122648-14-0; **2b** (X = 1,2,3,4,5-Me, R = Me), 122871-05-0; **2b** (X = 1,2,3,4,5-H, R = Ph), 122648-15-1; **2b** (X = 1,2,3,4,5-H, R = Me),

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122648-16-2; **3a** (X = 1,2,3,4,5-Me, R = Ph), 122648-24-2; **3a** (X = 1,2,3,4,5-Me, R = Me), 95344-72-2; **3a** (X = 1,2,4,5-Me, R = Ph), 95344-74-4; **3b** (X = 1,2,3,4,5-Me, R = Ph), 122648-18-4; **3b** (X = 1,2,3,4,5-Me, R = Me), 122648-20-8; **3b** (X = 1,2,3,4,5,6-Me, R = Me), 122648-22-0; **4a** (X = 1,2,3,4,5-Me, R = Me), 122741-55-3; **4a** (X = 1,2,4,5-Me, R = Ph), 122742-51-2; **4b** (X = 1,2,3,4,5-Me, R = Ph), 122648-25-3; **4b** (X = 1,2,3,4,5-Me, R = Me), 122648-26-4; $Re(CO)_5Br$, 14220-21-4; $[(C_6H_6)Re(CO)_3]AlCl_3Br$, 122648-27-5; $(C_6Me_7)Re(CO)_3$, 122648-28-6; Ph_4AsCN, 21154-65-4; Et_4NCN, 13435-20-6; PBu_3, 998-40-3; $CH(CO_2Me)_2^-$, 13435-20-6.

Mono(pentamethylcyclopentadienyl) Complexes of Cerium(III). Synthesis, Molecular Structure, Thermal Stability, and Reactivity of $(C_5Me_5)CeX_2$ (X = 2,6-Di-*tert*-butylphenoxo, $CH(SiMe_3)_2$, and $N(SiMe_3)_2$) Complexes

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Reaction of $Ce(OAr)_3$[1] (**1**) with LiR (R = C_5Me_5, 1,3-diphenyl-2-methylindene) affords novel $RCe(OAr)_2$ (R = C_5Me_5, **2**; R = 1,3-diphenyl-2-methylindene, **3**) compounds. Metathesis of the remaining aryloxide ligands in **2** with bulky main-group alkyl and amide compounds ($LiCH(SiMe_3)_2$ and $NaN(SiMe_3)_2$) provide neutral $C_5Me_5CeR_2$ complexes (R = $CH(SiMe_3)_2$, **5**; R = $N(SiMe_3)_2$, **6**). Compound **5** is a polymerization catalyst for ethylene but not for propylene. Compounds **2** and **6** disproportionate in solution with formation of equilibrium mixtures containing $C_5Me_5CeX_2$, $(C_5Me_5)_2CeX$, and CeX_3 complexes. Structural studies on **2**, **5**, and **6** show monomeric, formally five-coordinate compounds in the solid state. Compound **2** crystallizes in the monoclinic space group $P2_1$ with $a = 9.575$ (1) Å, $b = 17.026$ (2) Å, $c = 11.530$ (1) Å, $\beta = 112.02$ (1)°, and $Z = 2$. Compound **5** crystallizes in the hexagonal space group $P6_3$ with $a = 18.477$ (2) Å, $c = 15.991$ (3) Å, and $Z = 6$. Compound **6** crystallizes in the monoclinic space group $P2_1/c$ with $a = 19.252$ (6) Å, $b = 13.430$ (4) Å, $c = 12.503$ (3) Å, $\beta = 90.28$ (2)°, and $Z = 4$. All compounds display interesting secondary interactions of the metal with C–H and/or Si–C bonds in the solid state.

Introduction

The last decade, organometallic compounds of group 3 and lanthanide elements with unprecedented structural features and spectacular reactivity have been reported.[2] Especially worth mentioning are methane activation and β-methyl transfer reactions with lutetium compounds $(C_5Me_5)_2LuR$.[3] Lanthanide compounds $[(C_5Me_5)_2LnH]_2$ (Ln = La, Nd, Sm, Lu) have been shown to be extremely active catalysts for olefin hydrogenation and ethylene polymerization reactions.[4]

The reported chemistry deals mainly with cyclopentadienyl and substituted cyclopentadienyl compounds with the bis(pentamethylcyclopentadienyl) compounds $(C_5Me_5)_2LnR$ as the most extensively studied.[2] The two bulky pentamethylcyclopentadienyl ligands strongly influence the reactivity. An outstanding feature of this specific geometry is a dramatic improvement of stability, thus allowing detailed kinetic and mechanistic studies. However, the reactivity can also be decreased by the two bulky ligands. For example, propylene is neither polymerized nor oligomerized by $(C_5Me_5)_2ScMe$, whereas oligomers do form when the cyclopentadienyl ligands are bridged, e.g., by a $SiMe_2$ group.[5] The effect of the bridge is to open the wedge of the $(C_5Me_5)_2ScMe$ compound, thus allowing the propylene molecules to enter the coordination sphere and insert repeatedly into the Sc–C bond. It was shown by Marks et al. that ring-bridged hydrides, $[Me_2Si(C_5Me_4)_2LnH]_2$ (Ln = Nd, Sm, Lu), are ca. 10 times more active for the polymerization of ethylene than the corresponding $[(C_5Me_5)_2LnH]_2$ hydrides.[4b] This observation was also attributed to an increase of the coordination space around the metal by bridging the C_5Me_5 rings.

With these dramatic spatial effects in mind, we reasoned that mono(pentamethylcyclopentadienyl) complexes $(C_5Me_5)LnX_2$ may show interesting chemistry and we decided to investigate compounds of the type $(C_5Me_5)LnX_2$ (X = alkoxide, amide, carbyl). Because of our experience with bis(pentamethylcyclopentadienyl) derivatives of early

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(1) In this paper the following abbreviations are used: Ln = lanthanide or group 3 element; Ind* = 1,3-diphenyl-2-methylindenyl; OAr = 2,6-di-*tert*-butylphenoxo.

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