which is however not always reflected in lattice constants of alloys.[31] The present data imply perhaps an even larger effective metallic radius. In any case the metallic radius of gadolinium appears to be a totally unreliable benchmark.

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Registry No. YCl, 14530-75-7; YBr, 17655-40-2; Y_2Cl_3, 73728-21-9; Y_2Br_3, 73728-20-8; YCl_3, 10361-92-9; YBr_3, 13469-98-2; Y, 7440-65-5.

Supplementary Material Available: Tables of structure factor amplitudes (2 pages). Ordering information is given on any current masthead page.

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Spectroscopic Study on the Interaction of Tricyclopentadienides of Lanthanoid Elements with Metal Carbonyl Derivatives. 2.[1] Lewis Basicity of Nitric Oxide in Organometallic Nitrosyl Derivatives and Structures of Their Adducts with Tricyclopentadienylsamarium

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Received November 2, 1979

The Lewis basicity of nitric oxide, NO, in metal nitrosyl derivatives, $(\eta^5\text{-}C_5H_5)Cr(CO)_2NO$, $[(\eta^5\text{-}C_5H_5)FeNO]_2$, $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$, $(\eta^5\text{-}CH_3C_5H_4)_3Mn_3(NO)_4$, and $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)NO]_2$, has been studied by interaction of these complexes with the Lewis acid tricyclopentadienylsamarium, Cp_3Sm. IR spectra of the reaction mixtures displayed bands diagnostic of Cp_3Sm coordinated to terminal, two-metal bridging, and three-metal bridging NO. The order of the Lewis basicity of nitric oxide toward Cp_3Sm was terminal NO $\gtrsim$ two-metal bridging NO $\sim$ three-metal bridging NO. The proportion of cis-bridged isomers was increased by adding Cp_3Sm to $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$. $(\eta^5\text{-}CH_3C_5H_4)_3Mn_3(NO)_4$ was synthesized by refluxing a benzene solution of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)NO]_2$.

Nitric oxide, NO, forms a variety of complexes which are structurally and electronically similar to metal carbonyl derivatives.[2] However, only a few compounds with bridging nitrosyls have been subjected to structural elucidation.[3,4] Of particular interest in the study of organometallic compounds with bridging nitrosyls is the possibility of NO scrambling similar to the widely recognized phenomenon of CO scrambling.[5] For instance, it has been claimed that $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ shows a cis–trans equilibrium in solutions similar to the case of isoelectronic $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$.[6] So far, infrared spectroscopy has played a major role in the study of this kind of bridged–nonbridged and/or cis–trans equilibrium of metal carbonyl and nitrosyl derivatives in solutions. Of particular importance is the work of Shriver and his group who have employed IR spectra to study the influence of group 3 Lewis acids on bridge–terminal equilibria of metal carbonyl derivatives in solution.[7,8] Because of the isoelectronic nature of NO^+ to CO, the ligand NO in organometallic nitrosyl compounds is expected to display similar Lewis basicity, and therefore Lewis acids might provide valuable insight into the structures and equilibria of organometallic nitrosyl derivatives in solutions. However, only a few studies have so far been made on the Lewis basicity of ligand NO in nitrosyl metal derivatives.[9] The present study was undertaken to investigate the Lewis basicity of NO for three kinds of ligation modes, that is, terminal, two-metal bridged, and three-metal bridged ligation, and to elucidate structures and equilibria between organometallic nitrosyls and the hard Lewis acid tricyclopentadienylsamarium, $(\eta^5\text{-}C_5H_5)_3Sm$.[10]

Experimental Section

All reactions were carried out under a purified nitrogen atmosphere.[11] All solvents were distilled under a nitrogen atmosphere from calcium chloride or sodium benzophenone ketyl. Sampling techniques and IR spectral measurements have been described elsewhere.[1]

The nitrosyl derivatives $(\eta^5\text{-}C_5H_5)Cr(CO)_2NO$, $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$, and $[(\eta^5\text{-}C_5H_5)FeNO]_2$ were synthesized according to literature methods.[9,12,13] Manganese nitrosyl derivatives were synthesized

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Table I. Nitrosyl and Carbonyl Stretching Frequencies for Adducts of Organometallic Nitrosyl Derivatives with Cp_3Sm

parent compd	ν(NO), cm^{-1} (terminal)	ν(NO), cm^{-1} (-NO-Sm)	ν(NO), cm^{-1} (two-metal bridge)	ν(NO), cm^{-1} (>NO-Sm)	ν(NO), cm^{-1} (three-metal bridge)	ν(NO), cm^{-1} (⋗NO-Sm)	ν(CO), cm^{-1} (terminal)
$(\eta^5\text{-}C_5H_5)Cr(CO)_2NO$ (I)^a	1667 vs						2022 vs 1943 vs
I + Cp_3Sm (1:5)	1667 w	1590 vs					2042 vs 2022 w 1973 vs 1943 w
$[(\eta^5\text{-}C_5H_5)FeNO]_2$ (II)^b			1506 s				
II + Cp_3Sm (1:5)			1506 s	1430 m			
$(\eta^5\text{-}CH_3C_5H_4)_3Mn_3(NO)_4$ (III)^a			1540 vs 1490 vs		1335 m		
III + Cp_3Sm (1:5)			1540 vs 1500 s	1400 s	1343 m	1210 m	

^{a} Dichloromethane solution. ^{b} Benzene solution.

Table II. Nitrosyl and Carbonyl Stretching Frequencies for $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$, $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)NO]_2$, and Their Adducts with Cp_3Sm

parent compd and mole ratio	ν(NO), cm^{-1} (terminal)	ν(NO), cm^{-1} (-NO-Sm)	ν(NO), cm^{-1} (two-metal bridge)	ν(NO), cm^{-1} (>NO-Sm)	ν(CO), cm^{-1} (two-metal bridge)	ν(CO), cm^{-1} (>CO-Sm)	ν(CO), cm^{-1} (terminal)
$[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ (IV)^a	1730 w 1670 vs		1510 s				
1:1^a	1735 w 1670 vs	1620 w	1510 s				
1:2	1730 w 1670 vs	1620 m	1515 s	1430 w			
1:5	1720 m 1682 vs 1670 vs	1620 s	1520 s, br	1430 m			
1:10	1720 m 1682 vs 1670 vs	1620 s	1520 s, br	1430 m			
$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)NO]_2$ (V)^b	1712 vs		1520 s		1795 vs		1965 vs
1:10^b	1715 vs	1665 vw	1520 s		1797 vs	1745 vw	1965 vs
parent^c	1714 s		1518 m		1795 s		1957 s
1:1^c	1712 s	1690 w, sh	1520 m, br		1793 s	1740 m	1990 w, sh 1960 s
1:3^c	1713 s	1690 m	1520 m, br		1795 s	1740 s	1990 m 1960 s
parent^a	1715 vs		1515 m, br		1790 s		1970 s
1:1^a	1715 s	1690 m	1520 m		1790 s	1740 m	1970 s
1:1.1^a	1715 m	1685 s	1530 m, br		1795 m, br	1740 s	1990 s, br
1:1.2^a		1685 s	1530 m, br		1795 m, br	1740 s	1990 s, br
1:1.5^a		1685 s	1530 m, br		1800 w, br	1740 s	1992 s, br
1:4^a	1705 w, sh	1685 s	1530 m, br		1805 vw, br	1740 s	1995 s, br
1:7^a	1705 w	1685 s	1530 m		1805 vw, br	1740 s	1995 s, br
1:10^a	1705 m	1685 s	1530 m		1805 vw, br	1740 s	1995 s, br

^{a} Dichloromethane solution. ^{b} Tetrahydrofuran solution. ^{c} Benzene solution.

from less expensive $(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_3$ instead of expensive $(\eta^5\text{-}C_5H_5)Mn(CO)_3$; $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)NO]_2$ was synthesized by King's method.[12a] However, the procedure to synthesize trinuclear manganese nitrosyl derivative by King and Bisnette and by Kolthammer and Legzdins gives a low yield and is rather lengthy. Therefore, the following method was developed to synthesize $(\eta^5\text{-}CH_3C_5H_4)_3Mn_3(NO)_4$: 1.0 g of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)NO]_2$ was dissolved in 50 mL of benzene. After being refluxed for 13 h, the resulting dark green solution was filtered and the solvent was partially removed under reduced pressure. Then 20 mL of petroleum ether was added and the mixture was stored in a refrigerator overnight to afford a dark green precipitate. The precipitate was washed two times with 10 mL of petroleum ether and vacuum dried; yield 0.4 g (59%). Anal. Calcd for $(CH_3C_5H_4)_3Mn_3(NO)_4$: C, 41.40; H, 4.05; N, 10.73. Found: C, 41.54; H, 3.96; N, 10.60. Tricyclopentadienylsamarium, Cp_3Sm, was also synthesized by the literature method.[14]

Results of spectral measurements are summarized in Tables I and II.

Results and Discussion

The Lewis Basicity of the Ligand NO. The Lewis basicity of the ligand NO in organometallic nitrosyl derivatives was investigated by interacting Cp_3Sm as a Lewis acid with the following compounds: $(\eta^5\text{-}C_5H_5)Cr(CO)_2NO$ (I) for terminal NO, $[(\eta^5\text{-}C_5H_5)FeNO]_2$ (II) for two-metal bridging NO, and $(\eta^5\text{-}CH_3C_5H_4)_3Mn_3(NO)_4$ (III) for three-metal bridging NO, respectively. The reactions of these metal nitrosyl derivatives with Cp_3Sm were conducted with a 1:5 mole ratio in dichloromethane or in benzene. $(\eta^5\text{-}C_5H_5)Cr(CO)_2NO$ (I) gave rise to a new peak shifted to about 77 cm^{-1} lower frequency upon addition of a five times excess of Cp_3Sm in dichloromethane, and two carbonyl stretching peaks were shifted to higher frequencies.[9] Addition of diethylamine to this mixture regenerated the original IR spectrum of I in the ν(CO) and ν(NO) region. Therefore, the peak shifted to lower frequency is positively assigned to the ν(NO) mode in the $-NO\text{-}SmCp_3$ bond. Cp_3Sm caused about a 4.6% decrease in frequency upon terminal coordination to the terminal NO.

$[(\eta^5\text{-}C_5H_5)FeNO]_2$ (II), in which two NO groups symmetrically bridge a Fe–Fe double bond (a),[15] and a fivefold excess of Cp_3Sm were mixed in benzene. The mixture showed an

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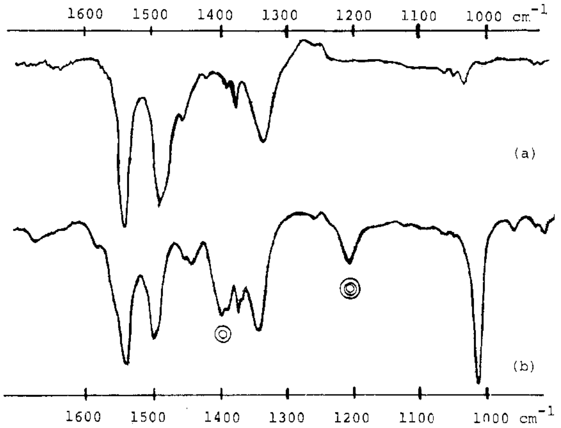
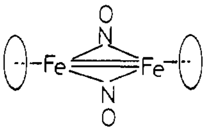
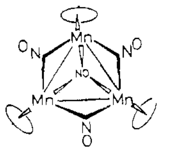


Figure 1. Infrared spectra of (a) $(\eta^5\text{-}CH_3C_5H_4)_3Mn_3(NO)_4$ and (b) its adducts with Cp_3Sm in CH_2Cl_2: (three circles) denotes NO stretch in ⋗NO–$SmCp_3$; (two circles) denotes NO stretch in >NO–$SmCp_3$.

additional medium-intensity peak at 1430 cm^{-1} besides a strong peak at 1506 cm^{-1} due to bridging nitrosyl stretch of uncoordinated compound II. As the peak at 1430 cm^{-1} disappeared upon addition of diethylamine, this peak was assigned to ν(NO) of the >NO–$SmCp_3$ bond. The frequency decrease by adduct formation is 76 cm^{-1}.



a



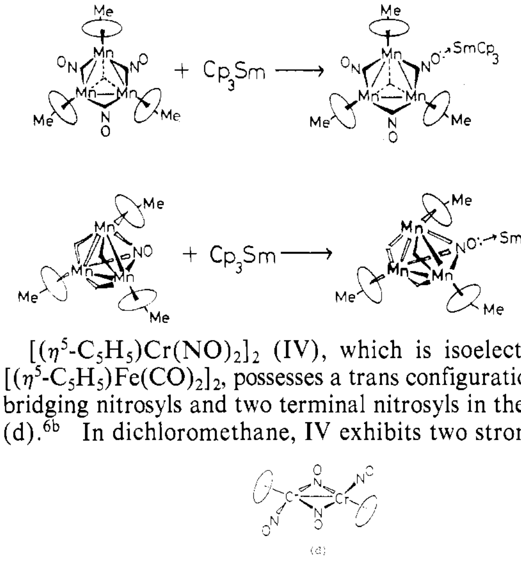
b

Kolthammer and Legzdins demonstrated that $(\eta^5\text{-}CH_3C_5H_4)_3Mn_3(NO)_4$ (III) is isostructural with its cyclopentadienyl analogue, $(\eta^5\text{-}C_5H_5)_3Mn_3(NO)_4$ (III′),[12b] which possesses three two-metal bridging NO's and one three-metal bridging NO (b).[16] On the basis of this virtual C_{3v} symmetry, two ν(NO) peaks, (A_1 + E), due to doubly bridging NO and one ν(NO) peak due to triply bridging NO are expected. The IR spectrum of III displays three peaks in the bridging nitrosyl stretching region in dichloromethane (Figure 1a).[12b] The higher frequency two peaks are assignable to ν(NO) of two-metal bridging NO and the lowest frequency peak to ν(NO) of three-metal bridging NO.[12a] Addition of a fivefold excess of Cp_3Sm produced two new peaks at 1400 (s) and 1210 (m) cm^{-1} and shifted the peak at 1490 cm^{-1} to 1500 cm^{-1} and the peak at 1335 cm^{-1} to 1343 cm^{-1}. When diethylamine was injected to this mixture, the original ν(NO) spectrum was regenerated. The peak at 1400 cm^{-1} is assignable to ν(NO) in the >NO–$SmCp_3$ bond and the peak at 1210 cm^{-1} to ν(NO) in ⋗NO–$SmCp_3$. The frequency decrease of ν(NO) by adduct formation is 120 cm^{-1} for three-metal bridging NO and 90 cm^{-1} for two-metal bridging NO.

The frequency decrease of ν(NO) by adduct formation with Cp_3Sm via the oxygen atom was about 9% for three-metal bridging NO, about 6% for two-metal bridging NO, and about 5% for terminal NO.

Next we examined the idea of establishing the order of the Lewis basicity of terminal NO, two-metal bridging NO, and three-metal bridging NO by changing the Cp_3Sm ratio to parent metal nitrosyl derivatives. First comparison was made for two-metal bridging NO and three-metal bridging NO by employing III as a parent compound. The mole ratio of Cp_3Sm was varied from 1:1.7 to 1:10. A clear spectral change was observed for the 1:2 reaction. A weak to medium intensity peak was detected at 1400 cm^{-1} and a weak peak was generated at 1210 cm^{-1}. With increasing Cp_3Sm concentration, intensities of these two peaks increased with almost equal rate and the intensities of the three ν(NO) bands of the parent complex decreased. At the same time, the peaks at 1490 and 1335 cm^{-1} were shifted to higher frequencies. Although the peak at 1540 cm^{-1} underwent no appreciable shift upon increasing the Cp_3Sm concentration, it became asymmetric and possessed an additional feature in its higher frequency side. On the basis of the relative intensities of two peaks at 1540 and 1490 cm^{-1} for parent complex and of the insensitivity of the peak at 1540 cm^{-1} to adduct formation, the peak at 1540 cm^{-1} is assigned to E mode of ν(NO) and the peak at 1490 cm^{-1} to A_1 mode.

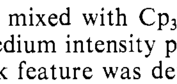
Appearance of two peaks assignable to ⋗NO–$SmCp_3$ and >NO–$SmCp_3$ at the same time for a 1:2 mole ratio indicates that there is no significant difference between the Lewis basicity of three-metal bridging NO's and two-metal bridging NO's to the Lewis acid, Cp_3Sm. If Cp_3Sm interacts with one of the bridging NO's (two-metal bridge or three-metal bridge), the electron density on the manganese atoms is decreased by the inductive effect of the NO–$SmCp_3$ bond and thus ν(NO) due to remaining NO should shift to higher frequencies. Therefore, the observation that both ν(NO) for three-metal bridging NO's and for two-metal bridging NO's shift to higher frequencies with the increase of Cp_3Sm concentration indicates that two types of Cp_3Sm interaction to NO occurred at the same time in parallel as is illustrated in (c).



(c-1)

(c-2)

$[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ (IV), which is isoelectronic with $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, possesses a trans configuration with two bridging nitrosyls and two terminal nitrosyls in the solid state (d).[6b] In dichloromethane, IV exhibits two strong peaks at 1670 and 1512 cm^{-1}, which are assignable to antisymmetric terminal and bridging nitrosyl stretchings. In addition, a weak broad band is detectable at around 1735 cm^{-1}, which is assigned to the symmetric terminal NO stretch of the cis isomer.[6] The problem of this cis–trans equilibrium in solutions will be discussed in a later section, but at present attention is focused on the Lewis basicity of the terminal and bridging nitrosyls in IV. When IV was mixed with Cp_3Sm in a 1:1 ratio in CH_2Cl_2, a weak to medium intensity peak was produced at 1620 cm^{-1} and a weak feature was detected at 1430 cm^{-1}, although it was difficult to estimate the intensity of this peak because of the interference with two weak bands at 1440 and 1422 cm^{-1} due to Cp_3Sm. By the injection of diethylamine to this solution, these two peaks disappeared. On the basis of this experiment and the findings described in the previous section, the peak at 1620 cm^{-1} was assigned to terminal NO stretch in the –NO–$SmCp_3$ bond and the band at 1430 cm^{-1} to two-metal bridge NO stretch in the >NO–$SmCp_3$ bond. With increasing Cp_3Sm concentration, the intensities of these



(d)

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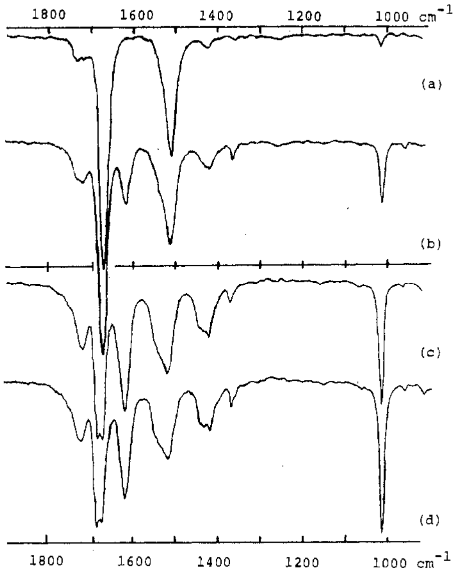
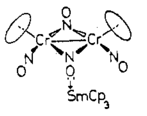


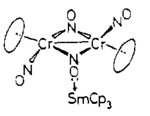
Figure 2. Infrared spectral change with the increase of Cp_3Sm: (a) $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$; (b) $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$:$Cp_3Sm$ = 1:2; (c) $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$:$Cp_3Sm$ = 1:5; and (d) $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$:$Cp_3Sm$ = 1:10 in CH_2Cl_2.

two peaks increased with almost equal rate. These results suggest that the tendency of terminal nitrosyl to form adducts with the hard Lewis acid, Cp_3Sm, is at an almost equal level with that of two-metal bridging nitrosyl.

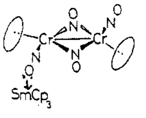
Structures of the Adducts of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ and $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)NO]_2$ in Solutions. Marks et al. and Calderon et al. demonstrated by IR and NMR spectra that $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ (IV) exists as a bridged cis and trans equilibrium mixture in solutions.[6] Because of the discrete bridged trans configuration of IV in the solid state,[6b] the conversion from the trans structure to the cis structure is believed to proceed via nonbridged intermediates as in the case of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$.[5] Figure 2 illustrates IR spectral changes with increasing Cp_3Sm concentration. Noteworthy changes are (i) one strong new peak was generated at 1682 cm^{-1} for a Cp_3Sm mole ratio greater than 1:5, (ii) the intensity of the symmetric NO stretch increased, as it was shifted from 1735 to 1720 cm^{-1} by adduct formation (exact estimate of the shift was impossible because the symmetric NO stretch at 1735 cm^{-1} in the parent compound IV was broad and of poor quality), (iii) the peak at 1510 cm^{-1} due to bridging NO stretch shifted to 1520 cm^{-1} with significant asymmetric broadening to its higher frequency side, and (iv) the band intensities due to NO stretches of $-NO-SmCp_3$ and $>NO-SmCp_3$ increased. All of these spectral changes were cancelled by injecting diethylamine into this solution. On this basis, it is concluded that adduct formation of Cp_3Sm with the oxygen atom in NO is responsible for these spectral changes. As was described in the previous section, there is no significant difference between the Lewis basicity of terminal NO and that of two-metal bridging NO's since 1:1 adducts are formed between either terminal NO or bridging NO and Cp_3Sm, (e) and (f). From the consideration of simple dipole moment model on (e) and (f) together with the results on the adduct formation between the bridging CO of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and AlR_3,[7a] two sets of NO stretching patterns are expected for (e) and (f). In the coordination of bridging NO to Cp_3Sm (e), one terminal NO stretch should be shifted to higher frequency by the inductive effect of the $>NO-Sm$ bond and two bridging NO stretches should be seen, one of which should shift to lower frequency and the other to higher frequency (pattern I). In the terminal coordination (f), two terminal NO stretches are expected, one of which should be shifted to lower frequency by adduct formation, and one bridging NO stretch which should be shifted to higher frequency by inductive effect of the $-NO-Sm$ bond (pattern II). The peak at 1682 cm^{-1} observed for a Cp_3Sm to IV ratio greater than 5:1, the broad feature at around 1520 cm^{-1}, and the peak at 1430 cm^{-1} are assigned to pattern I, whereas the peak at 1670 cm^{-1}, the peak at 1620 cm^{-1}, and the broad feature at around 1520 cm^{-1} are assigned to pattern II. In pattern II (terminal coordination), one of the terminal NO stretches underwent no detectable shift upon adduct formation. In this adduct, the terminal NO which is responsible for the peak at 1670 cm^{-1} is on the chromium atom which is remote from the $Cr-NO-Sm$ group, and this NO is less susceptible to the change of electron density on the chromium atom than is bridging NO.



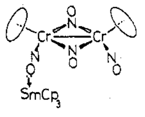
(e-1)



(e-2)



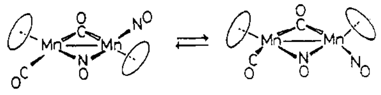
(f-1)



(f-2)

The increase in the intensity of symmetric terminal NO stretch (1725 cm^{-1}) indicates that the proportion of cis isomers (e-1) and/or (f-2) increased from parent to 1:1 adducts. The asymmetric line shape of two-metal bridged NO shifted to higher frequency indicates that the solution contains at least four species, e-1, e-2, f-1, and f-2, and that the higher frequency shifts of two-metal bridged NO for these species by adduct formation are somewhat different.

$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)NO]_2$ (V) exhibits four bands at 1970 (vs), 1790 (vs), 1715 (vs), and 1515 (s) cm^{-1} in the ν(CO) and ν(NO) region for dichloromethane solution. These bands are assigned to terminal carbonyl stretch, bridging carbonyl stretch, terminal nitrosyl stretch, and bridging nitrosyl stretch, respectively, on the basis of the IR spectra of the relevant carbonyl and nitrosyl derivatives.[3,4,6,7,9,12,15] Marks and Kristoff demonstrated by temperature-dependent proton NMR that $[(\eta^5\text{-}C_5H_5)Mn(CO)NO]_2$ (V′), which should have the same skeletal structure as that of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)NO]_2$ (V), exists as a mixture of dissymmetric cis and trans isomers in solutions (g).[4] To study the effect of the lanthanoid Lewis acid on this equilibrium, V was mixed in three different solvents with various mole ratios of Cp_3Sm. The spectral changes upon mixing with Cp_3Sm were most trivial in THF. Only two weak extra peaks were observed at 1745 and 1665 cm^{-1}, which were assigned to bridging CO stretch in the $>CO-Sm$ bond and to terminal NO stretch in the $-NO-Sm$ bond, respectively, for 1:10 reaction of V to Cp_3Sm. Basic tetrahydrofuran blocked the Lewis acid site on the samarium atom in Cp_3Sm and hindered the acid–base adduct formation between V and Cp_3Sm.

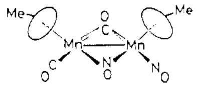


(g)

In benzene, three new peaks appeared at 1990, 1740, and 1690 cm^{-1} upon mixing V with Cp_3Sm at 1:3 and 1:6 ratios. The peak at 1690 cm^{-1} is assignable to a terminal NO stretch of the $-NO-Sm$, the peak at 1740 cm^{-1} to bridging CO stretch in $>CO-Sm$, and the peak at 1990 cm^{-1} to a terminal CO stretch shifted to higher frequency by adduct formation via bridging carbonyl in the trans isomer or to a terminal CO stretch of increased proportion of the cis isomer. In this solvent, two types of adduct formation, one with bridging CO and the other with terminal NO, were again observed as in the case of IV.

The spectral change with an increase of Cp_3Sm concentration was most drastic in CH_2Cl_2 and was similar to that reported by Crease and Legzdins.[9] Higher frequency shifts of the terminal carbonyl and the bridging carbonyl stretches for carbonyl groups not coordinated to Cp_3Sm were especially sensitive to Cp_3 concentration. The terminal NO stretch at 1715 cm^{-1} due to parent compound disappeared for Cp_3Sm to V ratios greater than 1.5:1, while the bridging carbonyl stretch for the bridging carbonyl not coordinated to Cp_3Sm was still detected for Cp_3Sm to V ratios greater than 10:1. A medium-intensity peak clearly appeared at 1705 cm^{-1} for Cp_3Sm to V ratio greater than 7:1. An attempt to locate unambiguously the peak due to bridging NO stretch for the >NO–Sm bond was unsuccessful. Injection of diethylamine into this solution regenerated the original spectrum in the ν(CO) and ν(NO) region. General spectral changes upon the addition of Cp_3Sm indicate that Cp_3Sm interacts preferentially with terminal nitrosyl and bridging carbonyl rather than bridging nitrosyl.[9]

The medium-intensity peak at 1705 cm^{-1} observed for a Cp_3Sm to V ratio greater than 7:1 is assigned to terminal NO stretch in the –NO–Sm bonded 1:2 adduct, where Cp_3Sm interacts with both bridging CO and terminal NO. This assignment is substantiated by the investigation of the peak at 1740 cm^{-1} due to bridging carbonyl stretch in the >CO–Sm bond; the peak possesses a shoulder on the higher frequency side and this shoulder could result from the shift of a bridging carbonyl stretch in the >CO–Sm bond when Cp_3Sm forms a 1:2 adduct via bridging CO and terminal NO. The fact that a weak peak due to bridging carbonyl stretch shifted to higher frequency was detected even for 10:1 reaction suggests that there still exists a small amount of the 1:1 adduct in solution, where the bridging carbonyl is directed in the same direction as those of two methylcyclopentadienyl rings as illustrated in (h). In this cis configuration, approach of bulky Cp_3Sm to bridging carbonyl should be somewhat deterred. From these experimental results, it is concluded that at higher concentrations of Cp_3Sm, three types of adducts, 1:1 with terminal NO, 1:1 with bridging CO, and 1:2 with both terminal NO and bridging CO, coexist in the CH_2Cl_2 solution. However, it is difficult to get any detailed insight into the influence of Lewis acid on the cis–trans equilibrium of V in solutions other than those described above, because compound V and its adduct are devoid of terminal carbonyl stretches characteristic of cis isomers, and attempts to get a proton NMR spectrum in suitable solvents have been unsuccessful.



(h)

Conclusion

In the present work, the Lewis basicity of the nitric oxide ligand has been demonstrated to be a general phenomenon for terminal, two-metal bridge NO, and three-metal bridged NO. The order of the Lewis basicity of NO for these ligation modes with respect to Cp_3Sm is somewhat different from that of carbonyl ligands with respect to group 3 Lewis acids.[8] The order is terminal NO ($\gtrsim$bridging CO) $\gtrsim$ two-metal bridged NO $\sim$ three-metal bridged NO. The low Lewis basicity of bridging NO is presumably responsible for the formation of only 1:1 adducts for $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$ and $(\eta^5\text{-}CH_3C_5H_4)_3Mn_3(NO)_4$. The observed increase in the proportion of the cis-bridged isomer upon adding Cp_3Sm to the nitrosyl bridged system, $[(\eta^5\text{-}C_5H_5)Cr(NO)_2]_2$, is analogous to the increase in the proportion of cis isomer when AlR_3 is added to the isoelectronic metal carbonyl, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$.

Registry No. I, 36312-04-6; II, 52124-51-3; III, 66795-25-3; IV, 36607-01-9; V, 73636-54-1; Cp_3Sm, 1298-55-1.

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Circularly Polarized Luminescence Studies of Mixed-Ligand Lanthanide Complexes Having the General Formula Tb(pyridine-2,6-dicarboxylic acid)$_m$(L-malic acid)$_n$, Where m = 0–3 and n = 0–2

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Circularly polarized luminescence (CPL) spectroscopy has been used to study the mixed-ligand complexes formed between Tb(III), dipicolinic acid (DPA), and L-malic acid (MAL). Complexes having the general formula of $Tb(DPA)_m(MAL)_n$ were prepared, where m = 0–3 and n = 0–2. At low pH, the observed CPL was found to arise from bidentate MAL coordination, but a drastic change in CPL line shape near pH 7 was interpreted to imply terdentate MAL bonding to Tb(III) above this pH. The complexes are mononuclear at all pH values, thus enabling certain conclusions to be drawn regarding relations between the observed CPL spectra and plausible solution structures.

Introduction

Chiroptical techniques enable one to probe the solution stereochemistry of metal complexes, and circular dichroism (CD) of metal d–d transitions has been employed to obtain detailed information regarding the structures of a wide variety of transition-metal complexes in solution.[1] Analogous studies of chiral lanthanide complexes have been attempted,[2] but the results of these investigations are tainted by uncertainities regarding the actual structures of the complexes and low signal-to-noise ratios. The CD is difficult to measure except at high lanthanide ion concentrations owing to the small extinction coefficients of the f–f transitions,[3] and it is usually

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