

## SPECTROSCOPIC STUDY OF THE INTERACTION OF TRICYCLOPENTADIENIDES OF LANTHANOID ELEMENTS WITH METAL CARBONYL DERIVATIVES. I

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### Summary

The interaction of samarium tricyclopentadienide,  $Cp_3Sm$ , with a diverse series of metal carbonyl derivatives has been investigated by IR and  $^1H$  NMR spectroscopy, and the variability of Lewis base sites in manganese carbonyl derivatives has been studied in terms of the charge on the manganese atom and the  $\pi$ -accepting ability of the ligands in these derivatives. In the series  $BrMn(CO)_{5-x}L_x$ , the oxygen atom functioned as the Lewis base site, while the manganese atom was the site of the Lewis basicity in anions of the type  $[Mn(CO)_{5-x}L_x]^-$  ( $x = 0, 1, 2$ ;  $L = P(OPh)_3$ ). The reactivity of the carbonyl oxygen atom in the series  $Me_{4-y}Sn[Mn(CO)_5]_y$  ( $y = 1, 2, 3$ ) was in the order:  $MeSn[Mn(CO)_5]_3 > Me_2Sn[Mn(CO)_5]_2 > Me_3Sn-Mn(CO)_5$ ;  $Cp_3Sm$  induced an upfield shift of the methyl proton NMR signal in these Sn–Mn compounds on adduct formation. Attempts to induce shifts of the terminal carbonyls to bridging positions in  $Mn_2(CO)_{10}$ ,  $[Mn(CO)_4P(OPh)_3]_2$ , and  $H_3Mn_3(CO)_{12}$  led instead to complexation at terminal carbonyl ligands.

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The Lewis basicity of metal carbonyl derivatives has now been well established through intensive studies, especially by Shriver's group [1]. Although much attention has been directed toward the Lewis basicity of carbonyl ligands, the basicity of the transition metal also has to be considered in the case of some metal carbonyl derivatives. One interesting example was reported by Burlich and Petersen for the  $[CpW(CO)_3]^-$  anion: this anion formed a Lewis acid–base complex via the oxygen atom with  $AlPh_3$ , while a complex was formed via the tungsten atom with  $InPh_3$  [2]. In this case, the Lewis base site changed as the nature of the Lewis acid employed changed [2]. This example provided the motivation for the present study. That is, a given Lewis acid, which usually tends to form a bond to a carbonyl oxygen, will prefer the transition metal atom to the oxygen atom of the carbonyl if: (1) a neutral metal carbonyl deri-

vative can be reduced to an anion, and/or (2) the Lewis basicity of the transition metal is increased by the accumulation of negative charge on the metal atom, and/or (3) when the carbonyl group(s) is substituted for weaker  $\pi$ -accepting ligand(s) and the Lewis basicity of the oxygen atom in the carbonyl is influenced by the enhanced localization of electrons in the metal-carbon bond [3]. To test these generalizations, we have employed a selected Lewis acid, samarium tricyclopentadienide,  $\text{Cp}_3\text{Sm}$ , and two series of manganese carbonyl derivatives  $\text{BrMn}(\text{CO})_{5-x}\text{L}_x$  and  $[\text{Mn}(\text{CO})_{5-x}\text{L}_x]^-$  ( $x = 0, 1, 2$ ;  $\text{L} = \text{P}(\text{OPh})_3$ ), as the Lewis bases. The reasons for the choice of a lanthanoid complex as a Lewis acid are twofold: First, the strong tendency of  $\text{Cp}_3\text{Sm}$  to form  $\text{Sm}-\text{O}$  bonds with terminal and bridging carbonyls was demonstrated recently by Legzdins and Crease [4]. Second, very few metal-metal bonds between a transition element and a lanthanoid element are known [4,5]. It was hoped that the present study would provide a good general procedure for the synthesis of complexes containing such bonds, thus offering some additional chemistry of organolanthanoid compounds, a class of compounds of current interest in organometallic chemistry [6,7].

## Experimental

All reactions were carried out under a nitrogen atmosphere [8]. Tetrahydrofuran was distilled from calcium hydride. Dichloromethane was dried over molecular sieves. Solvents were distilled under a nitrogen atmosphere.

### Materials

$\text{BrMn}(\text{CO})_5$  [9],  $\text{BrMn}(\text{CO})_3[\text{P}(\text{OPh})_3]_2$  [10],  $[\text{Mn}(\text{CO})_5]^-$  [11],  $[\text{Mn}(\text{CO})_3\{\text{P}(\text{OPh})_3\}_2]^-$  [12],  $\text{Me}_3\text{Sn}-\text{Mn}(\text{CO})_5$  [11],  $\text{Me}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$  [11],  $\text{MeSn}[\text{Mn}(\text{CO})_5]_3$  [13],  $\text{H}_3\text{Mn}_3(\text{CO})_{12}$  [14],  $[\text{Mn}(\text{CO})_4\text{P}(\text{OPh})_3]_2$  [15] and  $\text{Cp}_3\text{Sm}$  [16] were prepared by literature methods.  $\text{Mn}_2(\text{CO})_{10}$ ,  $\text{Fe}(\text{CO})_5$ ,  $\text{Fe}_2(\text{CO})_9$ , and  $\text{Fe}_3(\text{CO})_{12}$  were purchased from Strem Chemicals, Inc.  $\text{BrMn}(\text{CO})_4\text{P}(\text{OPh})_3$  and  $[\text{Mn}(\text{CO})_4\text{P}(\text{OPh})_3]^-$  were prepared as follows: 550 mg (2 mmol) of  $\text{BrMn}(\text{CO})_5$  was dissolved in 60 ml of chloroform. To this was added 620 mg (2 mmol) of triphenyl phosphite with stirring. The mixture was stirred at room temperature for 20 h. The solvent was removed under reduced pressure to leave an orange-yellow oil. This oil was extracted with 20 ml of cold n-hexane, and the extract was left standing at room temperature for 1 h. After removing a yellow precipitate by filtration, the filtrate was concentrated to afford a pale yellow precipitate. This precipitate was collected on a frit, washed with two 5 ml portions of petroleum ether and vacuum-dried to give 0.5 g of  $\text{BrMn}(\text{CO})_4\text{P}(\text{OPh})_3$ .  $[\text{Mn}(\text{CO})_4\text{P}(\text{OPh})_3]^-$  was prepared by the reduction of  $\text{BrMn}(\text{CO})_4\text{P}(\text{OPh})_3$  with excess amount of 1% sodium amalgam in THF.  $[\text{Mn}(\text{CO})_5]^-$  and  $[\text{Mn}(\text{CO})_3\{\text{P}(\text{OPh})_3\}_2]^-$  were prepared by the reduction of  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{BrMn}(\text{CO})_3[\text{P}(\text{OPh})_3]_2$  in a similar manner [12]. The THF solution of these anions were separated from mercury by decantation or by filtration. Purity was checked by elemental analyses and/or IR spectroscopy.

### Spectral measurements

The reaction of  $\text{Cp}_3\text{Sm}$  with metal carbonyl derivatives was monitored by

TABLE 1

CARBONYL STRETCHING FREQUENCIES FOR PARENT CARBOONYLS AND THEIR ADDUCTS WITH Cp<sub>3</sub>Sm

Lewis base compound	Stoichiometry base/acid	$\nu(\text{CO})$ in THF (cm <sup>-1</sup> )	Time (h) <sup>a</sup>
BrMn(CO) <sub>5</sub>	—	2138w, 2047vs, 2008s	44
BrMn(CO) <sub>4</sub> L	—	2023s, 1936vs	
	—	2100s, 2020vs, 1975s	
	1/1	2020m, 1995s, 1953vs, 1936s(sh), 1900w	145
	1/10	2021m, 1992w(sh), 1960w(sh), 1936vs, 1900m	80
BrMn(CO) <sub>3</sub> L <sub>2</sub>	—	2067w, 1994vs, 1951s	
	1/1	2067w <sup>b</sup> , 2050w, 2002w, 1995vs, <sup>b</sup> 1952s <sup>b</sup> , 1900w	195
[Mn(CO) <sub>5</sub> Γ	—	2005w <sup>c</sup> , 1900vs, 1875vs(sh), 1865vs, 1830m	
	1/9	2020m, 1935s, 1900s, 1875s(sh), 1865vs, 1832m	60
	1/9	2020s, 1935vs, 1900m	113
[Mn(CO) <sub>4</sub> LLΓ	—	1962m, 1878s, 1850vs, 1805m	
	1/1	2080w, 2060w, 2030m(sh), 2020s, 1995s(sh), 1978vs, 1965(sh), 1935s, 1905s,	160
	1/13	2085w, 2022s, 1998m, 1965m(sh), 1936vs, 1900m, 1868m <sup>d</sup>	162
[Mn(CO) <sub>3</sub> L <sub>2</sub> Γ	—	1955w, 1920w, 1835vs, 1783vs	
	1/1	2022w, 1955vs, 1903s	90
	1/13	2020w, 1958vs, 1937s <sup>d</sup> , 1900s, 1868w <sup>d</sup>	42
MeSn[Mn(CO) <sub>5</sub> ] <sub>3</sub>	—	2109w, 2075s, 2012s, 1995vs	
	1/5	2110vw <sup>b</sup> , 2075s <sup>b</sup> , 2048m, 2012vs <sup>b</sup> , 1995s(sh) <sup>b</sup> , 1980s(sh), 1939m, 1910m(sh)	32
Me <sub>2</sub> Sn[Mn(CO) <sub>5</sub> ] <sub>2</sub>	—	2102w, 2089w, 2077s, 2005vs, 1980s(sh)	
	1/5	2102w <sup>b</sup> , 2094vw, 2076s <sup>b</sup> , 2046vw, 2022m(sh), 2005vs <sup>b</sup> , 1980s(sh) <sup>b</sup> , 1937m	
	—	2092m, 1990vs	
Me <sub>3</sub> Sn—Mn(CO) <sub>5</sub>	—	2092m <sup>b</sup> , 2020m, 1990vs <sup>b</sup> , 1938m, 1900vw	110
Fe <sub>3</sub> (CO) <sub>12</sub>	—	2110w, 2050vs, 2025m, 1865vw, 1830vw	
	1/10	2023s, 1998vs, 1960m, 1930w, 1905vw, 1786m	20
Fe(CO) <sub>5</sub>	—	2117vw, 2021vs, 1996vs	
	1/10	no reaction	67
Mn <sub>2</sub> (CO) <sub>10</sub>	—	2047s, 2010vs, 1980s	
	1/1	2047s <sup>b</sup> , 2010vs <sup>b</sup> , 1980s <sup>b</sup> , 1935m, 1910vw	70
	1/10	same as that of [Mn(CO) <sub>5</sub> Γ + Cp <sub>3</sub> Sm (1/9) at 60 h	
	—	2072w, 2021(s), 1995s(sh), 1978vs	
[Mn(CO) <sub>4</sub> L <sub>2</sub> ]	—	2072w <sup>b</sup> , 2020m <sup>b</sup> , 1995m(sh) <sup>b</sup> , 1978vs <sup>b</sup> , 1936m, 1900m	100
H <sub>3</sub> Mn <sub>3</sub> (CO) <sub>12</sub>	—	2080m, 2032vs, 2009s, 1982m	
	1/5	2115vw, 2047s, 2020s(sh), 2010vs <sup>b</sup> , 1982m <sup>b</sup> , 1938vs, 1905w(sh)	32

<sup>a</sup> Spectra in the left-hand column were measured at this time after mixing. <sup>b</sup> Peaks due to parent carbonyls. <sup>c</sup> Peaks due to unreduced parent carbonyl. <sup>d</sup> Peaks due to extra coordination of Cp<sub>3</sub>Sm.

TABLE 2

<sup>1</sup>H NMR SPECTRA OF MANGANESE CARBONYL DERIVATIVES AND THEIR SHIFTS INDUCED BY (C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>Sm

Compound	δ(τ) (ppm from CH <sub>2</sub> Cl <sub>2</sub> (TMS))	Upfield shift (ppm)
MeSn[Mn(CO) <sub>5</sub> ] <sub>3</sub> <sup>a</sup>	3.94(8.61) <sup>b</sup> , 4.51(9.18) <sup>c</sup> , 2.32(6.99) <sup>d</sup> , 3.46(8.13) <sup>e</sup> , 1.67(6.34) <sup>e</sup>	0.57
Me <sub>2</sub> Sn[Mn(CO) <sub>5</sub> ] <sub>2</sub> <sup>a</sup>	4.40(9.07) <sup>b</sup> , 5.21(9.88) <sup>c</sup> , 2.32(6.99) <sup>d</sup> , 3.46(8.13) <sup>e</sup> , 1.67(6.34) <sup>e</sup>	0.81
Me <sub>3</sub> SnMn(CO) <sub>5</sub> <sup>a</sup>	4.78(9.45) <sup>b</sup> , 2.32(6.99) <sup>d</sup> , 3.46(8.13) <sup>e</sup> , 1.67(6.34) <sup>e</sup>	
H <sub>3</sub> Mn <sub>3</sub> (CO) <sub>12</sub> <sup>f</sup>	(23.7) <sup>g</sup>	

<sup>a</sup> Solvent CH<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup> Methyl proton signal (parent). <sup>c</sup> Methyl proton signal (adduct). <sup>d</sup> C<sub>5</sub>H<sub>5</sub> proton signal (center peak). <sup>e</sup> THF proton signal originally coordinated to Cp<sub>3</sub>Sm (center peak). <sup>f</sup> Solvent THF. <sup>g</sup> Hydride proton signal.

IR spectroscopy. A typical preparation of a sample solution was as follows: 0.1 mmol of a metal carbonyl derivative and Cp<sub>3</sub>Sm were placed in a 50 ml three-necked flask. To this was added 20 ml of THF through a rubber cap attached to the flask, and the mixture was stirred at room temperature. Spectra were recorded on a JASCO IR-701G spectrometer with an expanded scale using a well-matched pair of NaCl windowed solution cells (0.1 mm path length). The sample cell was evacuated and then filled with nitrogen. The sample solution was taken from the reaction flask using a syringe and was injected into the cell through a serum cap on the cell. The reaction was monitored over a period of one week.

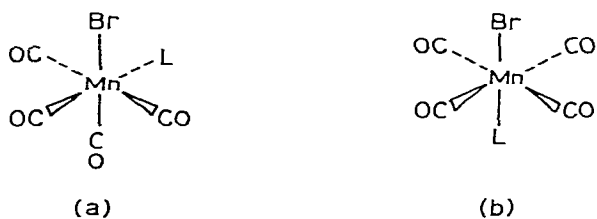
<sup>1</sup>H NMR spectra were recorded on Hitachi-Perkin-Elmer R-20B and R-24A (60 MHz) spectrometers. TMS and dichloromethane were employed as internal standards. THF and dichloromethane were also used as solvents. In the case of H<sub>3</sub>Mn<sub>3</sub>(CO)<sub>12</sub>, <sup>1</sup>H NMR spectra could be obtained for a THF solution, even though the literature suggests Fe(CO)<sub>5</sub> was the only effective solvent for NMR spectroscopy of H<sub>3</sub>Mn<sub>3</sub>(CO)<sub>12</sub> [14]. The results are summarized in Table 1 and 2.

## Results and discussion

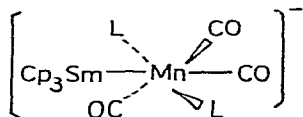
The reaction of Cp<sub>3</sub>Sm with BrMn(CO)<sub>5-x</sub>L<sub>x</sub> (x = 0, 1, 2; L = P(OPh)<sub>3</sub>) in THF was studied for 1/1 mixtures and for solutions with a large excess of Cp<sub>3</sub>Sm. ν(CO) peaks for this series of compounds were shifted to lower frequencies by the addition of Cp<sub>3</sub>Sm, suggesting that Cp<sub>3</sub>Sm interacted with the oxygen atom of the carbonyl ligand [4b] \*. Reaction was completed within 30 h for BrMn(CO)<sub>5</sub>, but proceeded only slightly for BrMn(CO)<sub>3</sub>L<sub>2</sub> even after one week. The reactivity of BrMn(CO)<sub>4</sub>L toward Cp<sub>3</sub>Sm is intermediate relative to those of BrMn(CO)<sub>5</sub> and BrMn(CO)<sub>3</sub>L<sub>2</sub>. Using a large excess of Cp<sub>3</sub>Sm with these derivatives, the equilibrium did not shift, but except for BrMn(CO)<sub>4</sub>L, it caused rapid decomposition of the manganese carbonyls. These findings indicate that the triphenyl phosphite group(s) is a deterrent to the complexation of Cp<sub>3</sub>Sm

\* Possible interaction of Cp<sub>3</sub>Sm with Br may not be overlooked. However, this type of interaction should cause a slight increase in ν(CO).

at the oxygen atom in the carbonyl, the bulky triphenyl phosphite group(s) hindering the approach of  $\text{Cp}_3\text{Sm}$  to the carbonyl(s).  $\text{BrMn}(\text{CO})_5$  yielded two distinct  $\nu(\text{CO})$  peaks  $70\text{--}110\text{ cm}^{-1}$  lower than those of the parent carbonyl upon complexation with  $\text{Cp}_3\text{Sm}$  (Fig. 1a). This observation suggests that the complex is formed through the axial CO group (*trans* to Br). This range of lower frequency shifts may be compared to the shift ( $60\text{ cm}^{-1}$ ) of  $\nu(\text{CO})$  for  $(\pi\text{-C}_5\text{H}_4\text{CH}_3)\text{Mn}(\text{CO})_3$  and  $\text{R}_3\text{Ln}$  [4b], where the interaction occurred via the terminal carbonyl oxygen atom. The reaction of  $\text{Cp}_3\text{Sm}$  with  $\text{BrMn}(\text{CO})_3\text{L}_2$  gave a weak extra feature at  $1900\text{ cm}^{-1}$  assignable to the complex (Fig. 1b). The reaction of  $\text{Cp}_3\text{Sm}$  with  $\text{BrMn}(\text{CO})_4\text{L}$  in a 1/1 ratio gave a complex  $\nu(\text{CO})$  spectrum 30 h after mixing owing to the presence of unreacted parent compound. An interesting feature of this reaction is that the spectral change with reaction time was different for 1/1 and 10/1 mixtures as is illustrated in Fig. 1c and 1d.  $\text{BrMn}(\text{CO})_4\text{L}$  is supposed to possess a *cis* structure (a) in solution [17,18]. For this structure, three different kinds of Lewis base sites for CO are possible. The change in  $\nu(\text{CO})$  spectra with reaction time and/or with the change of mole ratio suggests that the CO functioning as the Lewis base site towards  $\text{Cp}_3\text{Sm}$  was changed or the *cis* structure of  $\text{BrMn}(\text{CO})_4\text{L}$  was changed to the *trans* structure (b) during the reaction.



The interaction of  $\text{Cp}_3\text{Sm}$  with a series of  $[\text{Mn}(\text{CO})_{5-x}\text{L}_x]^-$  anions caused higher frequency shifts of the  $\nu(\text{CO})$  peaks upon complexation. These shifts in  $\nu(\text{CO})$  ranged from  $80$  to  $120\text{ cm}^{-1}$  for the lowest carbonyl stretching peaks in the parent anion; this range of shifts is similar to the shift of  $55\text{ cm}^{-1}$  for the interaction of  $[\text{CpW}(\text{CO})_3]^-$  with  $\text{InPh}_3$  where the complex was formed through the tungsten atom [2]. The present results reflect the charge transfer from the manganese to the samarium atom. The reactivity of this series of anions with  $\text{Cp}_3\text{Sm}$  in a 1/1 ratio was in the order:  $[\text{Mn}(\text{CO})_3\text{L}_2]^- > [\text{Mn}(\text{CO})_4\text{L}]^- > [\text{Mn}(\text{CO})_5]^-$  based on the time required for complete spectral change. The observation of three terminal CO stretching bands together with the higher frequency shifts for the complex between  $\text{Cp}_3\text{Sm}$  and  $[\text{Mn}(\text{CO})_3\text{L}_2]^-$  supports the bonding model  $[\text{Cp}_3\text{Sm}-\text{Mn}(\text{CO})_3\text{L}_2]^-$  depicted in (c) on the basis of the local symmetry prediction for  $\nu(\text{CO})$  bands and of known structures of  $\text{R}_3\text{Sn}-\text{Mn}(\text{CO})_3\text{L}_2$  and  $\text{BrMe}_2\text{Sn}-\text{Mn}(\text{CO})_3(\text{PPh}_3)_2$  [12,19]. In the case of the reaction



(c)

with excess  $\text{Cp}_3\text{Sm}$  ( $\text{Cp}_3\text{Sm}/[\text{Mn}(\text{CO})_3\text{L}_2]^- = 13/1$ ), two extra peaks were

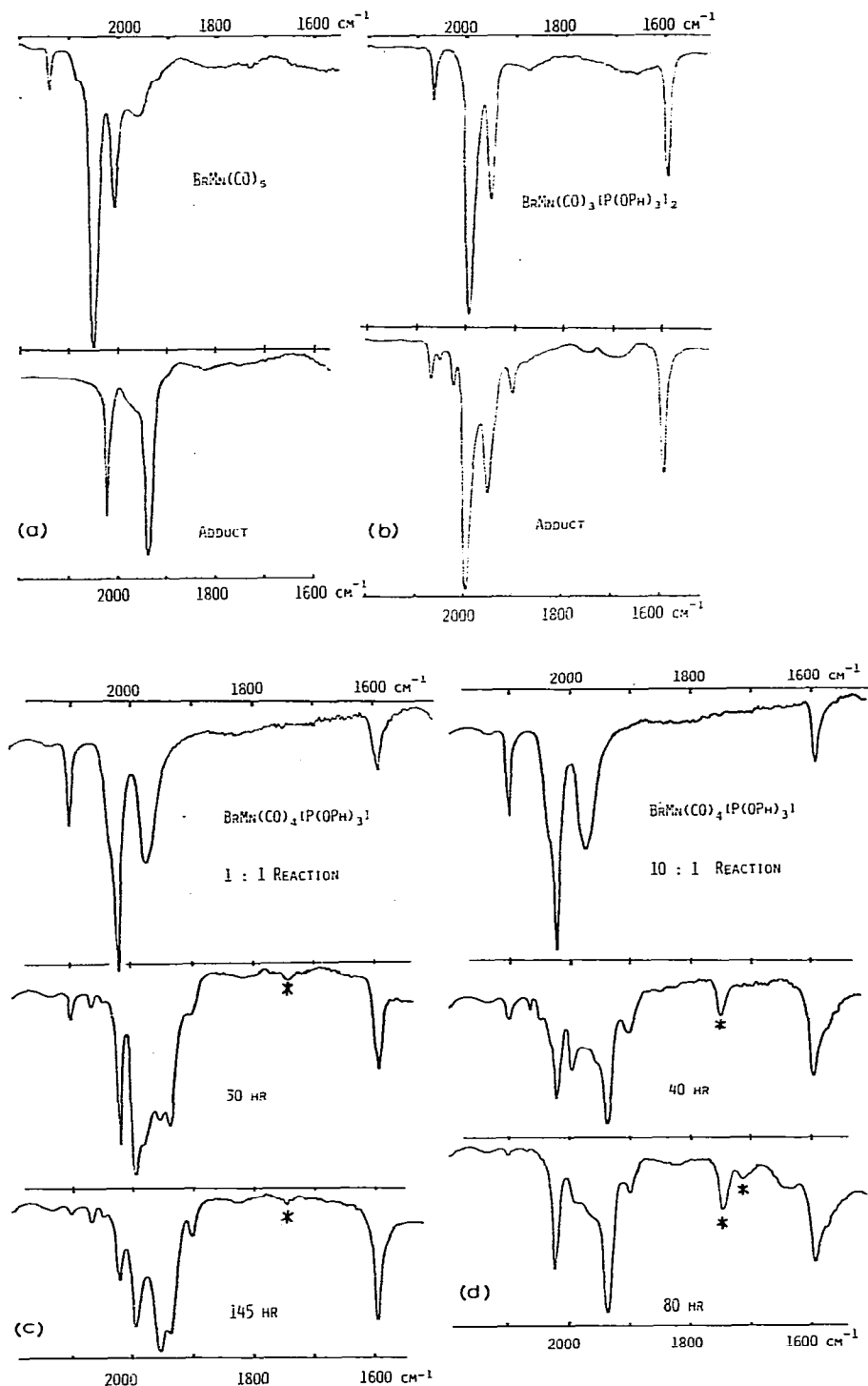


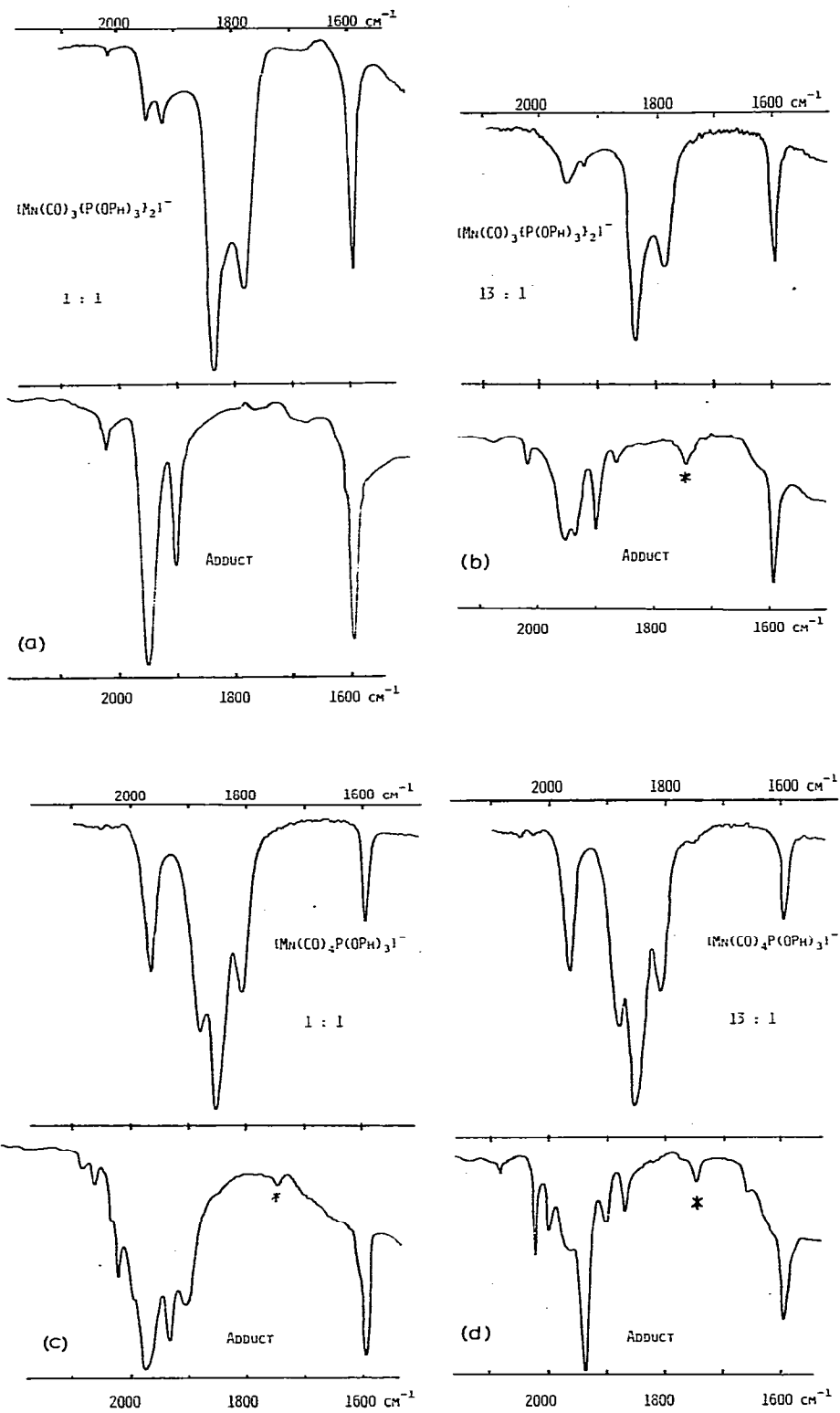
Fig. 1. Infrared spectra in  $\nu(\text{CO})$  region for  $\text{BrMn}(\text{CO})_{5-x}\text{L}_x$  and their adducts with  $\text{Cp}_3\text{Sm}$  in THF. (a)  $\text{BrMn}(\text{CO})_5$ , (b)  $\text{BrMn}(\text{CO})_3\text{L}_2$ , (c) and (d)  $\text{BrMn}(\text{CO})_4\text{L}$ ; spectral change with reaction time and mole ratio. \* denotes peaks due to  $\text{Cp}_3\text{Sm}$ .

observed at 1937 and 1868  $\text{cm}^{-1}$  (Fig. 2a and 2b). These two peaks can be assigned to  $\nu(\text{CO})$  peaks for the species in which additional  $\text{Cp}_3\text{Sm}$  is coordinated to the oxygen of a carbonyl group in the  $[\text{Cp}_3\text{Sm}-\text{Mn}(\text{CO})_3\text{L}_2]^-$  complex.

The interaction of  $\text{Cp}_3\text{Sm}$  with the  $[\text{Mn}(\text{CO})_4\text{L}]^-$  anion in a 1/1 ratio shifted the three strong carbonyl stretching peaks in the 1800–1900  $\text{cm}^{-1}$  region to the 1900–2100  $\text{cm}^{-1}$  region, and eight terminal carbonyl stretching peaks were detected. For a 13/1 mole ratio of  $\text{Cp}_3\text{Sm}/[\text{Mn}(\text{CO})_4\text{L}]^-$ , seven terminal carbonyl stretching peaks were observed. Spectral change with reaction time of a 1/1 ratio was different from that for 13/1 as in the case of  $\text{BrMn}(\text{CO})_4\text{L} + \text{Cp}_3\text{Sm}$  (Fig. 2c and 2d). The observation of a peak at 1868  $\text{cm}^{-1}$  for the 13/1 reaction indicates again coordination of  $\text{Cp}_3\text{Sm}$  to a terminal carbonyl in  $[\text{Cp}_3\text{Sm}-\text{Mn}(\text{CO})_4\text{L}]^-$ .  $[\text{Mn}(\text{CO})_5]^-$  did not exhibit any detectable change even 93 h after mixing with  $\text{Cp}_3\text{Sm}$  in a 1/1 ratio. However, medium intensity peaks were observed at 2020 and 1935  $\text{cm}^{-1}$  18 h after mixing with 9/1 mole ratio of  $\text{Cp}_3\text{Sm}/[\text{Mn}(\text{CO})_5]^-$ , and the intensity of these two peaks increased with time. After 113 h, the resulting orange-brown solution showed three peaks at 2020s, 1935vs, and 1900m  $\text{cm}^{-1}$  (Fig. 2e), consistent with  $C_{4v}$  local symmetry structure for  $[\text{Cp}_3\text{Sm}-\text{Mn}(\text{CO})_5]^-$ . So far, we have not been able to obtain analytically pure samples of these adducts by precipitation with bulky cations such as  $(\text{Ph}_3\text{P})_2\text{N}^+$ .

The reactivity of a series of  $[\text{Mn}(\text{CO})_{5-x}\text{L}_x]^-$  anions with  $\text{Cp}_3\text{Sm}$  is thought to be dependent on the strength of the Lewis basicity and/or the Lewis base softness of the manganese atom in the respective anion, because it has already been established that  $\text{Cp}_3\text{Ln}$  is a soft Lewis acid [7]. The observed trend of Lewis basicity of the manganese atom can be understood in terms of the increased softness of the manganese atom; the negative charge on the manganese atom is increased by substitution of CO group(s) by the weaker  $\pi$ -accepting ligand,  $\text{P}(\text{OPh})_3$  [3] and by reduction of a neutral species to an anion. The present IR study clearly demonstrated the conditions necessary for facile metal–metal bond formation between a lanthanoid element and a transition atom. The program to prepare other compounds with metal–metal bonds between lanthanoid elements and transition elements based on this idea is now in progress, and a subsequent paper will soon appear.

So far much attention has been attracted to the dependence of the Lewis basicity of carbonyls on the bonding mode, that is, terminal or bridging ligation [1]; however, the dependence of carbonyl Lewis basicity on the number of metal atoms has not yet been a subject for investigation to our knowledge. This type of study was made for a series of  $\text{Me}_{4-x}\text{Sn}[\text{Mn}(\text{CO})_5]_x$  ( $x = 1, 2, 3$ ) derivatives. The reaction of  $\text{Cp}_3\text{Sm}$  with this series of compounds was examined for both THF and  $\text{CH}_2\text{Cl}_2$  solutions with 5/1 mole ratio. IR monitoring of the reaction for THF solutions demonstrated that new terminal CO stretching peaks appeared at lower frequencies, and unreacted parent manganese carbonyl derivatives still existed after 100 h for these three compounds.  $^1\text{H}$  NMR could be employed to estimate the exact degree of complexation for  $\text{CH}_2\text{Cl}_2$  solutions of these compounds, as  $\text{Cp}_3\text{Sm}$  caused upfield shifts of the methyl proton signals upon complexation (Fig. 3). The amounts of complexed manganese carbonyl derivatives after 24 h were 38% for  $\text{MeSn}[\text{Mn}(\text{CO})_5]_3$  and 12% for  $\text{Me}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$ , based on the peak height intensities of the methyl proton signals. Complexed  $\text{Me}_3\text{Sn}-\text{Mn}(\text{CO})_5$  was in such low concentration that it





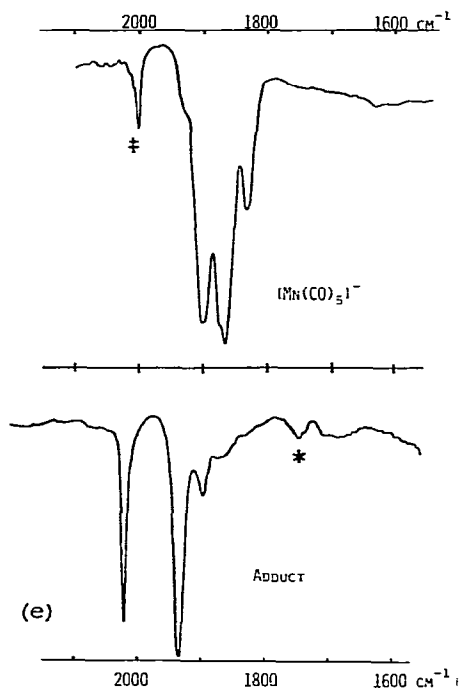
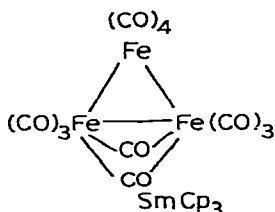
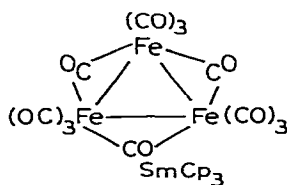


Fig. 2. Infrared spectra in  $\nu(\text{CO})$  region for  $[\text{Mn}(\text{CO})_{5-x}\text{L}_x]^-$  and their adducts with  $\text{Cp}_3\text{Sm}$  in THF. (a) and (b)  $[\text{Mn}(\text{CO})_3\text{L}_2]^-$ ; spectral change with mole ratio for  $\text{Cp}_3\text{Sm}$ . (c) and (d)  $[\text{Mn}(\text{CO})_4\text{L}]^-$ ; spectral change with mole ratio for  $\text{Cp}_3\text{Sm}$ . (e)  $[\text{Mn}(\text{CO})_5]^-$ . † denotes unreduced  $\text{Mn}_2(\text{CO})_{10}$  and \* denotes  $\text{Cp}_3\text{Sm}$ .

eluded observation even after 24 h. The reactivity of the CO groups for these three compounds to  $\text{Cp}_3\text{Sm}$  is thus established to be in the order:  $\text{MeSn}[\text{Mn}(\text{CO})_5]_3 > \text{Me}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2 > \text{Me}_3\text{Sn}-\text{Mn}(\text{CO})_5$ . In order to investigate the general validity of this finding for homonuclear systems,  $\text{Fe}(\text{CO})_5$ ,  $\text{Fe}_2(\text{CO})_9$ , and  $\text{Fe}_3(\text{CO})_{12}$  were employed.  $\text{Fe}(\text{CO})_5$  did not display spectral change even after 67 h. Instead, sample decomposition occurred after 90 h.  $\text{Fe}_3(\text{CO})_{12}$  showed distinct change by the interaction with ten times excess amount of  $\text{Cp}_3\text{Sm}$  in THF immediately after mixing. After 3 h of mixing, the reaction was completed; two weak peaks due to bridging carbonyls disappeared completely and a weak to medium intensity peak was observed at  $1786\text{ cm}^{-1}$ , which was assignable to a  $>\text{CO}-\text{SmCp}_3$  bond [4b,21]. In addition, two weak bands were present at  $1930$  and  $1905\text{ cm}^{-1}$  in the adduct (Fig. 4). If these two peaks are due to bridging carbonyls shifted to higher frequencies by complexation of  $\text{Cp}_3\text{Sm}$ , structure (e) is favored rather than (d) [20,21].



(d)



(e)

$\text{Fe}_2(\text{CO})_9$  and a ten-fold excess of  $\text{Cp}_3\text{Sm}$  were mixed in THF. After 8 h of stirring,  $\text{Fe}_2(\text{CO})_9$  was dissolved completely and afforded a transparent orange-red solution. The IR spectrum of this solution was in agreement with that of the solution of  $\text{Fe}_3(\text{CO})_{12}$  and  $\text{Cp}_3\text{Sm}$ . Apparently, the dinuclear iron framework was converted to a trinuclear framework by addition of  $\text{Cp}_3\text{Sm}$ . This type of oligomerization is not unusual for  $\text{Fe}_2(\text{CO})_9$ . For instance,  $\text{Fe}_2(\text{CO})_9$  is thermally converted to  $\text{Fe}_3(\text{CO})_{12}$  [22]. The observed trend in reactivity for iron carbonyl derivatives is:  $\text{Fe}_3(\text{CO})_{12} > \text{Fe}_2(\text{CO})_9 > \text{Fe}(\text{CO})_5$ , and this order of reactivity is in accord with that of the heteronuclear carbonyl case. Lower frequency shifts upon formation of a  $>\text{CO}-\text{Sm}$  bond were small compared with the shifts caused by  $\text{AlBr}_3$  with iron derivatives [20]. This observation indicates a weaker Lewis acidity for  $\text{Cp}_3\text{Sm}$  than for group III Lewis acids such as  $\text{AlR}_3$  [4b,20].

The reaction of  $\text{Cp}_3\text{Sm}$  with a series of polynuclear manganese carbonyl derivatives,  $\text{Mn}_2(\text{CO})_{10}$ ,  $[\text{Mn}(\text{CO})_4\text{L}]_2$ , and  $\text{H}_3\text{Mn}_3(\text{CO})_{12}$  was attempted with the hope of inducing the shift of a terminal carbonyl to a bridging position. The reaction took place easily for  $\text{H}_3\text{Mn}_3(\text{CO})_{12}$  and  $\text{Cp}_3\text{Sm}$  in THF. However, even after 60 h, no shift of terminal to a bridging position occurred, although complexation via terminal carbonyls took place. The parent carbonyl hydride gave rise to a  $^1\text{H}$  NMR signal at  $\tau = 23.7$  ppm in THF. However, repeated attempts to detect the signal in the  $\tau = 10-40$  ppm region were unsuccessful for the complex. A similar change in  $\nu(\text{CO})$  spectra was observed in  $\text{CH}_2\text{Cl}_2$ , but at a significantly slower rate than in THF. For  $[\text{Mn}(\text{CO})_4\text{L}]_2$ , the interaction with  $\text{Cp}_3\text{Sm}$  was studied for 1/1 and 1/10 mole ratios in THF. In a 1/1 mole ratio, the reaction was quite slow and no appreciable change was observed

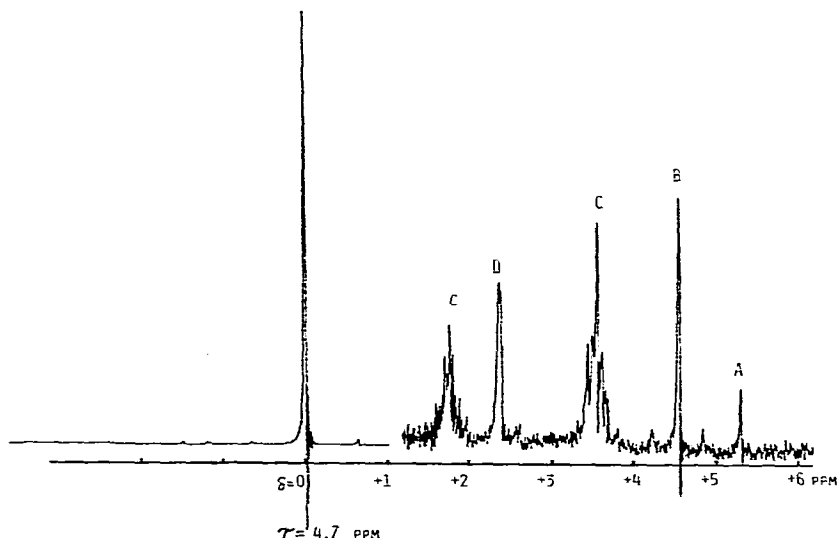


Fig. 3.  $^1\text{H}$  NMR spectrum of  $\text{Me}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$  and its adduct with  $\text{Cp}_3\text{Sm}$  in  $\text{CH}_2\text{Cl}_2$ . (A) Methyl proton signal for adduct; (B) methyl proton signal for parent  $\text{Me}_2\text{Sn}[\text{Mn}(\text{CO})_5]_2$ ; (C) THF signal which originally coordinated to  $\text{Cp}_3\text{Sm}$  and was freed from  $\text{Cp}_3\text{Sm}$  in  $\text{CH}_2\text{Cl}_2$  by adduct formation; (D)  $\text{C}_5\text{H}_5$  signal. Spectrum measured after 48 h.

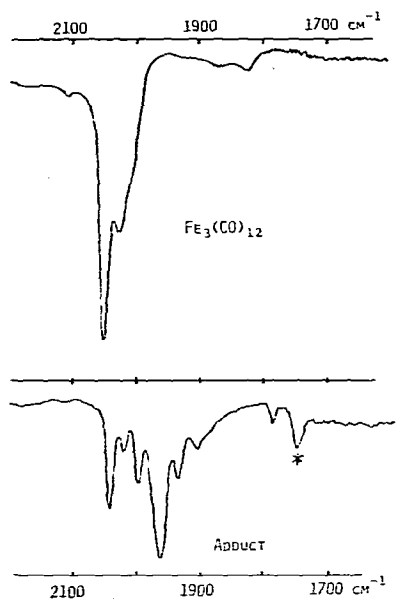


Fig. 4. Infrared spectra of  $\text{Fe}_3(\text{CO})_{12}$  and its adduct with  $\text{Cp}_3\text{Sm}$  in THF.

even after 44 h. In the case of a 1/10 mole ratio, two weak extra peaks were observed at 1936 and 1900  $\text{cm}^{-1}$ , assignable to a terminal  $-\text{CO}-\text{Sm}$  bond. However, the complex did not give rise to a peak assignable to a  $>\text{CO}-\text{Sm}$  bond even after 150 h. The interaction of  $\text{Mn}_2(\text{CO})_{10}$  with  $\text{Cp}_3\text{Sm}$  was studied for various mole ratios (from 1/1 to 1/10) in THF. In the case of a 1/10 mole ratio, the change in  $\nu(\text{CO})$  spectra was most drastic and, after 135 h, the spectrum was in complete agreement with the aforementioned spectrum of  $\text{Cp}_3\text{Sm} + [\text{Mn}(\text{CO})_5]^-$  (9/1 mole ratio, 60 h), indicating  $\text{Mn}_2(\text{CO})_{10}$  was reduced to  $[\text{Mn}(\text{CO})_5]^-$ . It was initially suspected that unreacted sodium might sublime together with  $\text{Cp}_3\text{Sm}$  when  $\text{Cp}_3\text{Sm}$  was purified by sublimation. Atomic absorption spectroscopy exhibited the presence of sodium in  $\text{Cp}_3\text{Sm}$  used for the reaction. However, the sodium content in ten times excess amount of  $\text{Cp}_3\text{Sm}$  to  $\text{Mn}_2(\text{CO})_{10}$  was insufficient to reduce  $\text{Mn}_2(\text{CO})_{10}$  completely to  $[\text{Mn}(\text{CO})_5]^-$ . Crease and Legzdins pointed out that an oxidation-reduction might have taken place in the reaction between  $(\text{C}_5\text{H}_4\text{CH}_3)_3\text{Nd}$  and  $(\pi\text{-C}_5\text{H}_5)_2\text{Sn}$  in benzene [4b]. The ability of  $\text{Cp}_3\text{Sm}$  to reduce  $\text{Mn}_2(\text{CO})_{10}$  to  $[\text{Mn}(\text{CO})_5]^-$  in some manner should not be overlooked, though the exact origin of the reducing behaviour has not yet been clarified.

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## References

- 1 D.F. Shriver, *J. Organometal. Chem.*, **94** (1975) 259 and references therein.
- 2 J.M. Butlitch and R.B. Petersen, *J. Organometal. Chem.*, **24** (1970) C65.
- 3 F. Basolo and R.G. Pearson, *Mechanisms of Inorganic Reactions*, Wiley, New York, 1967, Ch. 7.
- 4 (a) A.E. Crease and P. Legzdins, *J. Chem. Soc. Chem. Commun.*, (1972) 268; (b) A.E. Crease and P. Legzdins, *J. Chem. Soc. Dalton*, (1973) 1501; (c) A.E. Crease and P. Legzdins, *J. Chem. Soc. Chem. Commun.*, (1973) 775.
- 5 R.S. Marianelli and M.T. Durney, *J. Organometal. Chem.*, **32** (1971) C41.
- 6 R.G. Hayes and J.L. Thomas, *Organometal. Chem. Rev. A*, **7** (1971) 1.
- 7 T.J. Marks, *J. Organometal. Chem.*, **79** (1974) 181.
- 8 D.F. Shriver, *Manipulation of Air Sensitive Compounds*, McGraw-Hill, New York, 1969.
- 9 E.W. Abel and G. Wilkinson, *J. Chem. Soc.*, (1959) 1501.
- 10 R.J. Angelici, F. Basolo and A.J. Poë, *J. Amer. Chem. Soc.*, **85** (1963) 2215.
- 11 R.D. Gorsich, *J. Amer. Chem. Soc.*, **84** (1962) 2486.
- 12 S. Onaka, Y. Yoshikawa and H. Yamatera, *J. Organometal. Chem.*, **157** (1978) 187.
- 13 A.J. Thompson and W.A.G. Graham, *Inorg. Chem.*, **6** (1967) 1365.
- 14 S.F.G. Johnson, R.D. Johnson, J. Lewis and B.H. Robinson, *J. Organometal. Chem.*, **10** (1967) 195.
- 15 D. Drew, D.J. Darensbourg and M.Y. Darensbourg, *Inorg. Chem.*, **14** (1975) 1579.
- 16 J.M. Birmingham and G. Wilkinson, *J. Amer. Chem. Soc.*, **78** (1956) 42.
- 17 R.J. Angelici and F. Basolo, *J. Amer. Chem. Soc.*, **84** (1962) 2495.
- 18 H.K. Spendjian and I.S. Butler, *Inorg. Chem.*, **9** (1970) 1268.
- 19 S. Onaka, *Chem. Letters*, (1978) 1163.
- 20 J.S. Kristoff and D.F. Shriver, *Inorg. Chem.*, **13** (1974) 499.
- 21 D.F. Shriver, S. Onaka and D. Strobe, *J. Organometal. Chem.*, **117** (1976) 277.
- 22 J. Dewar and H.O. Gones, *Proc. Roy. Soc. (London)*, **A76** (1905) 558.