The Lewis Acidity of Organolanthanides.   Evidence for Isocarbonyl and Isonitrosyl Complex Formation

By A. E. CREASE and P. LEGZDINS*

(Department of Chemistry, The University of British Columbia, Vancouver 8, Canada)

Summary   A decrease in N–O and C–O stretching frequencies in the infrared spectra of transition-metal complexes in the presence of monomeric organolanthanides indicates adduct formation via the oxygen lone pair of electrons.

PRIMARILY aluminium[1] and organoaluminium compounds[2-5] have exhibited Lewis acid behaviour towards the oxygen atom of a carbon monoxide ligand, although two cases are known in which either a transition metal[6] or europium[7] fulfils this role.   We now report that some organolanthanides can act as Lewis acids not only towards the oxygen atom of a terminal or bridging carbonyl ligand, but also towards the oxygen atom of an appropriate terminal nitrosyl ligand.

Previous studies[8,9] have shown that Cp_3Ln complexes (where $Cp = C_5H_5^-$ and Ln = a lanthanide) form thermally stable 1:1 adducts with conventional Lewis bases such as Ph_3P, C_4H_8O, NH_3, and $C_6H_{11}NC$.   We have used selected Cp_3Ln compounds (i.e. Ln = Sm, Er, and Yb), and their MeCp analogues, as the Lewis acids towards the potential electron donors $[\pi\text{-}CpFe(CO)_2]_2$, $\pi\text{-}CpCr(NO)_2Cl$, and $\pi\text{-}Me\text{-}CpMn(CO)_3$ in dichloromethane.

The interaction of the lanthanide element with the oxygen atoms of the carbonyl and nitrosyl ligands to form isocarbonyl and isonitrosyl linkages, respectively, is shown by the i.r. data given in the Table.

Upon complex formation in CH_2Cl_2 both of the NO stretching frequencies in $\pi\text{-}CpCr(NO)_2Cl$ are lowered (e.g. 1818 to 1786 and 1712 to 1686 cm^{-1} for Cp_3Yb) thereby implying a weakening of the N–O bond as electrons are donated to the lanthanide.   The extent of complexation is dependent upon the metal employed.   For example, even though $(MeCp)_3Sm$ is present in excess, the spectral data

indicate the presence of a small amount of the uncomplexed nitrosyl compound, whereas for Cp_3Er and Cp_3Yb complete

I.r. spectra in the carbonyl and nitrosyl stretching region

Lewis base	Lewis acid[a]	CO and NO absorptions, cm^{-1}
(a) Nujol mulls		
$[\pi\text{-}CpFe(CO)_2]_2$		1955s, 1938s, 1752s
$[\pi\text{-}CpFe(CO)_2]_2$	2 $(MeCp)_3Sm$	2024s, 1980br, 1700br,s
$[\pi\text{-}CpFe(CO)_2]_2$	2 Cp_3Sm	2020s, 1985br, 1700br,s
(b) CH_2Cl_2 solutions		
$[\pi\text{-}CpFe(CO)_2]_2$[b]		2005s, 1958s, 1786s
$[\pi\text{-}CpFe(CO)_2]_2$	2 $(MeCp)_3Sm$	1993s, 1952m, 1772s, 1700w
$\pi\text{-}MeCpMn(CO)_3$		2018s, 1928br,s
$\pi\text{-}MeCpMn(CO)_3$	1 or 2 $(MeCp)_3Sm$	2018s, 1928br,s, 1868m
$\pi\text{-}MeCpMn(CO)_3$	Cp_3Er or Cp_3Yb	2018s, 1928br,s, 1868m
$\pi\text{-}MeCpMn(CO)_3$	Cp_2YbCl	2018s, 1928br,s
$\pi\text{-}CpCr(NO)_2Cl$		1818s, 1712s
$\pi\text{-}CpCr(NO)_2Cl$	> 2 $(MeCp)_3Sm$	1818sh, 1775s, 1712sh, 1676s
$\pi\text{-}CpCr(NO)_2Cl$	Cp_3Er	1786s, 1688s
$\pi\text{-}CpCr(NO)_2Cl$	Cp_3Yb	1786s, 1686s
$\pi\text{-}CpCr(NO)_2Cl$	Cp_2YbCl	1818s, 1712s
$\pi\text{-}CpCr(NO)_2Cl$	$(MeCp)_2YbCl$	1818s, 1784sh, 1712s, 1684sh

a Increasing the amount of Lewis acid beyond the indicated stoicheiometry produces no further changes in the spectra.   b See ref. 10.

complexation is observed as expected.   Further, it should be noted that Cp_2YbCl and $(MeCp)_2YbCl$ show no or very little adduct formation, respectively.   This observation is further supporting evidence for their existence in non-donor solvents as chlorine-bridged dimers.[11]

The interaction of the organolanthanides with the oxygen atom of a terminal carbonyl group is weaker than that previously reported[1,3,4] for various aluminium systems.

Consistent with group theoretical predictions of a lowered symmetry,[10] three bands are observed in the carbonyl stretching region of the i.r. spectrum when π-MeCpMn(CO)$_3$ and Cp$_3$Ln are treated in a 1:1 ratio. Two of the bands are unchanged from those of the parent carbonyl compound but a third band appears in all cases at 1868 cm^{-1}. (When aluminium is used as the acidic site in similar complexes, this latter absorption appears at approximately 1650 cm^{-1}.) The extent of complexation is dependent upon the metal used, and in both the terminal nitrosyl and carbonyl cases, dilution of the complex concentration below ca. 10^{-3}M causes partial dissociation of the adduct.

In an attempt to compare directly the basicities of NO and CO ligands, Fe(CO)$_2$(NO)$_2$ was utilized as a potential electron donor in CH$_2$Cl$_2$. However, even in the presence of an excess (> 2:1) of Cp$_3$Yb, no shifts in the carbonyl and nitrosyl stretching frequencies of the parent compound were observed. Evidently the strong bonding within the ligands in Fe(CO)$_2$(NO)$_2$ sufficiently reduces the electron density at the oxygen atoms to preclude adduct formation.

When [π-CpFe(CO)$_2$]$_2$ and (MeCp)$_3$Sm are mixed in a 1:2 ratio in benzene at room temperature, a bright red solid, whose elemental analysis is consistent with the formulation [π-CpFe(CO)$_2$]$_2$·2(MeCp)$_3$Sm, rapidly precipitates. The i.r. spectrum of this air-sensitive solid as a Nujol mull shows

shifts which are analogous to those exhibited by the known [π-CpFe(CO)$_2$]$_2$·2AlEt$_3$,[2] namely a shift to higher frequencies for the terminal CO stretches and a shift to lower frequency for the bridging CO stretch relative to those observed for the parent iron compound. These shifts are again smaller in magnitude for the samarium complex than for the aluminium complex, but they do indicate that the two adducts are quite probably isostructural with the Lewis acid being co-ordinated to the oxygen atom of the bridging carbonyl.[2] In solution, however, the adduct experiences almost complete dissociation as shown by its i.r. spectrum.

The Lewis acidity of monomeric organolanthanides can also be used further not only to form novel complexes with a variety of Lewis bases in which transition and main group metals are the basic sites, but also to simplify the n.m.r. spectra of complex organometallic molecules bearing appropriate donor ligands. The results of these studies will be presented in subsequent publications.

[1] R. B. Petersen, J. J. Stezowski, C. Wan, J. M. Burlitch, and R. E. Hughes, J. Amer. Chem. Soc., 1971, 93, 3532.
[2] N. J. Nelson, N. E. Kime, and D. F. Shriver, J. Amer. Chem. Soc., 1969, 91, 5173.
[3] J. C. Kotz and C. D. Turnipseed, Chem. Comm., 1970, 41.
[4] J. M. Burlitch and R. B. Petersen, J. Organometallic Chem., 1970, 24, C65.
[5] A. Alich, N. J. Nelson, and D. F. Shriver, Chem. Comm., 1971, 254.
[6] E. L. Brown and D. B. Brown, Chem. Comm., 1971, 67.
[7] T. J. Marks, J. S. Kristoff, A. Alich, and D. F. Shriver, J. Organometallic Chem., 1971, 33, C35.
[8] E. O. Fischer and H. Fischer, J. Organometallic Chem., 1966, 6, 141.
[9] M. Tsutsui, T. Takino, and D. Lorenz, Z. Naturforsch., 1966, 21b, 1.
[10] F. A. Cotton, A. D. Liehr, and G. Wilkinson, J. Inorg. Nuclear Chem., 1955, 1, 175.
[11] R. E. Maginn, S. Manastyrskyj, and M. Dubeck, J. Amer. Chem. Soc., 1963, 85, 672.