The Lewis Acidity of Organolanthanides. The Interaction of Cyclopentadienyl-lanthanides with some Carbonyl and Nitrosyl Complexes

By **Allan E. Crease** and **Peter Legzdins,*** Department of Chemistry, The University of British Columbia, Vancouver 8, Canada

The i.r. and ^{1}H n.m.r. spectra of a number of compounds containing sites of Lewis basicity change in the presence of selected cyclopentadienyl-lanthanides, R_3Ln. These spectral changes indicate that the lanthanides can act as Lewis acids towards bases such as bridging and terminal carbonyl ligands, terminal nitrosyl ligands, appropriate transition metals and some carbon–carbon triple bonds. Several solid adducts can be isolated and characterized. The preparation of the new compounds $R_2LnM(\pi\text{-}C_5H_5)(CO)_3$ [Ln = Dy, Ho, Er, or Yb; M = Mo or W] is described, and evidence for the existence of isocarbonyl linkages in these complexes is presented.

IN an earlier communication,[1] we briefly reported that some organolanthanides can function 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. This type of behaviour results in the formation of isocarbonyl and isonitrosyl linkages to the lanthanide element. In this paper we give a detailed account of these studies as well as the extension of the previous work to a variety of other base sites. Further, we describe the effect of the lanthanide Lewis acidity in some new compounds containing metal carbonyl anions as ligands.

Primarily aluminium and organoaluminium compounds [2] have exhibited the tendency to form isocarbonyl bonds, although two cases are known in which either a transition metal [3] or europium [4] behaves in an analogous manner. We have employed selected R_3Ln [$R = C_5H_5$ or MeC_5H_4; Ln = Nd, Sm, Gd, Dy, Ho, Er, or Yb] compounds as the Lewis acids towards potential electron donors such as bridging and terminal carbonyl ligands, terminal nitrosyl ligands, the metal atom in $(\pi\text{-}C_5H_5)_2WH_2$, and the carbon–carbon triple bond in phenylacetylene. The acid-base interactions were detected by i.r. and ^{1}H nuclear magnetic resonance spectroscopy, and adducts were isolated when possible. In addition, we have investigated complexes of the type $R_2LnM(\pi\text{-}C_5H_5)(CO)_3$ [Ln = Dy, Ho, Er, or Yb; M = Mo or W] for evidence of isocarbonyl behaviour.

EXPERIMENTAL

All chemicals used were of reagent grade or comparable purity. All reagents were either purchased from commercial suppliers or prepared according to reported procedures, and their purity was ascertained by elemental analyses and/or m.p. determinations. All solvents were dried (if necesary), distilled, and degassed just prior to use, and all manipulations were performed in an atmosphere of prepurified nitrogen.

I.r. spectra were recorded on a Perkin-Elmer 457 spectrophotometer and ^{1}H nuclear magnetic resonance spectra were recorded on a Varian Associates T60 spectrometer with tetramethylsilane being employed as an internal standard. Elemental analyses were carried out by Galbraith Laboratories, Knoxville, Tennessee, and Mr. P. Borda of this department.

Dicarbonyl(π-cyclopentadienyl)nitrosylmetal Compounds.—The compounds $(\pi\text{-}C_5H_5)M(CO)_2(NO)$ [M = Cr, Mo, or W] were all synthesized in an identical manner. The method of preparation, using the chromium complex as a typical example, was as follows. $Na[(\pi\text{-}C_5H_5)Cr(CO)_3]$ (1·77 g, 7·90 mmol) was suspended in diethyl ether (30 ml) and the mixture was cooled to 10 °C. Then, *N*-methyl-*N*-nitroso-*p*-toluenesulphonamide (1·81 g, 8·5 mmol) dissolved in diethyl ether (10 ml) were added slowly to the suspension, whereupon the reaction mixture evolved gas and darkened in colour. After the addition was complete, the reaction mixture was stirred for a further 15 min at 10 °C. The solvent was removed under vacuum and the remaining residue was sublimed [50 °C, 10^{-2} mmHg] onto an ice-cooled probe. Bright orange crystals of the desired product were thus obtained in at least 60% yield (Found: C, 41·3; H, 2·6; N, 6·8. $C_7H_5CrNO_3$ requires C, 41·4; H, 2·5; N, 6·9%). The molybdenum and tungsten compounds of comparable purity were obtained in similar yields. The physical and chemical properties of these complexes have been extensively described.[5]

The Tris(methylcyclopentadienyl)samarium–Octacarbonyldicobalt 2:1 *Adduct.*—$(C_5H_5Me)_3Sm$ (1·59 g, 4·10 mmol) was dissolved in toluene (30 ml) to produce a bright orange solution, and $Co_2(CO)_8$ (1·40 g, 4·10 mmol) was dissolved in toluene (15 ml) to produce a red-brown solution. The two solutions were filtered into a common flask and the mixture of filtrates was rapidly stirred. Within 20 min the solution became cloudy and a solid began to precipitate. After a further 2 h of stirring at room temperature, the reaction mixture was filtered and the yellow-orange solid thus obtained was washed thoroughly with toluene (5 × 20 ml) until the washings were colourless. The remaining bright yellow solid was dried *in vacuo* overnight. The yield (2·10 g) was virtually quantitative (Found: C, 46·8; H, 4·0; Sm, 26·3. $C_{22}H_{21}CoO_4Sm$ requires C, 47·3; H, 3·8; Sm, 26·9%).

The adduct is extremely sensitive to air and moisture, rapidly being converted to a green solid if exposed to moist air and even decomposing over a period of several days in an atmosphere of prepurified nitrogen. It is insoluble in non-polar organic solvents such as benzene, toluene, and hexane. It dissolves in polar solvents such as diethyl ether, tetrahydrofuran (THF), dichloromethane, and acetonitrile only with attendant dissociation, as indicated by the

---

[1] A. E. Crease and P. Legzdins, *J.C.S. Chem. Comm.*, 1972, 268.

[2] D. F. Shriver and A. Alich, *Co-ordination Chem. Rev.*, 1972, **8**, 15; D. F. Shriver, *Chem. in Britain*, 1972, **8**, 419 and references contained therein.

[3] E. L. Brown and D. B. Brown, *Chem. Comm.*, 1971, 67.

[4] T. J. Marks, J. S. Kristoff, A. Alich, and D. F. Shriver, *J. Organometallic Chem.*, 1971, **33**, C35.

[5] K. W. Barnett, *J. Organometallic Chem.*, 1972, **44**, 1.

appearance of the characteristic red-brown colour of $Co_2(CO)_8$ and the diagnostic bands of the latter species in the CO-stretching region of the i.r. spectrum of the solution.

The Tris(methylcyclopentadienyl)samarium–Bis[(π-cyclopentadienyl)dicarbonyliron] 2 : 1 Adduct.—$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ (0·49 g, 1·38 mmol) dissolved in benzene (15 ml) were added dropwise at room temperature to a stirred solution of $(MeCp)_3Sm$ (1·01 g, 2·68 mmol) dissolved in benzene (50 ml). Within a few minutes a solid began to precipitate. Stirring was continued for 2 h to ensure completion of the reaction. The reaction mixture was then filtered to obtain a bright red solid which was washed thoroughly with pentane (3 × 10 ml) and dried *in vacuo*. The solid was recrystallized from a dichloromethane–hexane solution to obtain red microcrystals of the adduct in 70% yield (Found: C, 51·1; H, 4·6; Fe, 9·5. $C_{25}H_{26}FeO_2Sm$ requires C, 53·2; H, 4·6; Fe, 9·9%). The low carbon analysis is not unexpected for this organolanthanide complex.[6]

The red compound is rapidly destroyed by air and moisture. It is thermally unstable above 120 °C at 10^{-1} mmHg, and attempts at vacuum sublimation of the complex give only low yields of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$. Further, the adduct is virtually insoluble in all common organic solvents except CH_2Cl_2 and THF, but once in solution it experiences almost complete dissociation as shown by its i.r. spectrum.

The Complexes $(cp)_2LnW(\pi\text{-}C_5H_5)(CO)$, *where* cp = C_5H_5 or C_5H_4Me, Ln = Dy, Ho, Er, or Yb.—The preparation of $(cp)_2YbW(\pi\text{-}C_5H_5)(CO)_3$ typefies the synthetic method employed to obtain all the $(cp)_2LnW(\pi\text{-}C_5H_5)(CO)_3$ compounds. A solution containing $Na[(\pi\text{-}C_5H_5)W(CO)_3]$ (1·00 g, 2·81 mmol) in THF (40 ml) was syringed into THF (40 ml) containing $(Cp)_2YbCl$ (0·956 g, 2·82 mmol). A precipitate formed immediately, and the resultant brown reaction mixture was stirred overnight at room temperature. The mixture was then centrifuged and the supernatant brown solution was decanted from the solid matter. The solution was concentrated under reduced pressure until crystals began to form, at which point it was cooled in an ice–salt bath for 2 h. The golden crystals thus formed were collected by filtration, washed with pentane (3 × 5 ml), and dried *in vacuo*. The desired product was obtained in 75% yield.

Analytical data for the complexes are summarized below.

Complex	Found (%)	Calculated (%)
$(C_5H_5)_2YbW(\pi\text{-}C_5H_5)(CO)_3$	C, 33·9; H, 2·4; Yb, 27·2	C, 34·0; H, 2·4; Yb, 27·2
$(C_5H_5)_2ErW(\pi\text{-}C_5H_5)(CO)_3$	C, 34·2; H, 2·7; Er, 26·4	C, 34·3; H, 2·4; Er, 26·5
$(C_5H_4Me)_2HoW(\pi\text{-}C_5H_5)(CO)_3$	C, 36·1; H, 3·3	C, 36·6; H, 2·9
$(C_5H_4Me)_2DyW(\pi\text{-}C_5H_5)(CO)_3$	C, 36·2; H, 3·0	C, 36·7; H, 2·9

All these complexes are air- and moisture-sensitive, and decompose at temperatures greater than 220 °C. They are readily soluble in donor solvents such as THF and dimethyl sulphoxide (DMSO), but are decomposed by halogenated solvents such as CH_2Cl_2.

$Er[(\pi\text{-}C_5H_5)Mo(CO)_3]_3,7H_2O$.—A solution containing $Na[(\pi\text{-}C_5H_5)Mo(CO)_3]$ (3·22 g, 12·0 mmol) in water (120 ml) was filtered into an aqueous solution (60 ml) containing $ErCl_3,6H_2O$ (1·27 g, 3·30 mmol). A solid immediately deposited. After stirring at room temperature for 15 min, the solid was collected by filtration and was washed with water (3 × 15 ml). The resulting tan solid was dried over P_4O_{10} *in vacuo* for one day. Yield, 1·65 g, 48% (Found: C, 28·0; H, 2·4. $C_{24}H_{29}ErMoO_{16}$ requires C, 28·0; H, 2·8%). The product is totally insoluble in water or common organic solvents and it does not sublime. Moreover, it decomposes within minutes upon exposure to air to yield detectable amounts of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$.

RESULTS AND DISCUSSION

Evidence for the Lewis Acid Behaviour of R_3Ln *Complexes.*—Previous studies[7,8] have shown that $(Cp)_3Ln$ complexes (where 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 utilized i.r. and n.m.r. spectroscopy (as well as elemental analyses where possible) to provide evidence that R_3Ln [R = C_5H_5 or C_5H_4Me] species can generally function as Lewis acids towards a variety of base sites. The following discussion is divided into sections dealing with each of the types of electron donors investigated.

(a) *Terminal Nitrosyl and Carbonyl Ligands.*—Upon complexation of $(\pi\text{-}C_5H_5)Cr(NO)_2Cl$ and R_3Ln in CH_2Cl_2, the i.r. spectrum (Table 1) shows that both the NO stretching frequencies 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 by the oxygen atom of the ligand to the lanthanide. The extent of complexation is dependent upon the lanthanide employed. For example, even though $(MeC_5H_4)_3Sm$ 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 complexation is observed as expected. Moreover, if an alternative solvent such as benzene is used, complete adduct formation with $(MeC_5H)_3Sm$ still does not occur.

It should also be noted that the magnitude of the shift to lower wavenumbers of the NO frequencies is relatively constant for all the lanthanide complexes which form isonitrosyl linkages. Consequently, this spectral technique can only provide qualitative information about the degree of complex formation and it cannot be employed to establish a quantitative scale of acidities for the R_3Ln species. Further, $(cp)_2YbCl$ and $(MeC_5H_4)_2YbCl$ 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.[9]

The interaction of the organolanthanides with the oxygen atom of a terminal carbonyl group is weaker than that previously reported[10–12] for various aluminium

---

[6] F. A. Hart, A. G. Massey, and M. S. Saran, *J. Organometallic Chem.*, 1970, **21**, 147.

[7] E. O. Fischer and H. Fischer, *J. Organometallic Chem.*, 1966, **6**, 141.

[8] M. Tsutsui, T. Takino, and D. Lorenz, *Z. Naturforsch.*, 1966, **21b**, 1.

[9] R. E. Maginn, S. Manastyrskyj, and M. Dubeck, *J. Amer. Chem. Soc.*, 1963, **85**, 672.

[10] R. B. Petersen, J. J. Stezowski, C. Wan, J. M. Burlitch, and R. E. Hughes, *J. Amer. Chem. Soc.*, 1971, **93**, 3532.

[11] J. C. Kotz and C. D. Turnipseed, *Chem. Comm.*, 1970, 41.

[12] J. M. Burlitch and R. B. Petersen, *J. Organometallic Chem.*, 1970, **24**, C65.

systems. Consistent with group theoretical predictions[13] of lowered symmetry, three bands are observed in the carbonyl stretching region of the i.r. spectrum when $(\pi\text{-}C_5H_4Me)Mn(CO)_3$ and $(cp)_3Ln$ are reacted in a 1 : 1 ratio. Two of the bands are unchanged from those of the parent compound, but a third band appears in all cases *ca.* 1868 cm^{-1}. [When aluminium[11] is used as the acidic site in similar complexes, this latter absorption appears at *ca.* 1660 cm^{-1}.] The extent of complexation is again dependent upon the metal employed and it cannot be enhanced by simply increasing the relative quantity of R_3Ln present. In both the terminal carbonyl and nitrosyl cases, dilution of the adduct concentration below *ca.* 10^{-3}M causes substantial dissociation.

TABLE 1

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

Lewis base	Lewis acid	CO and NO absorptions/cm^{-1}
(*a*) Nujol mulls		
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$		1955s, 1938s, 1752,
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$	2 $(C_5H_4Me)_3Sm$	2024s, 1980br,s, 1700br,s
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$	2 $(cp)_3Sm$	2020s, 1985br,s, 1700br,s
$Co_2(CO)_8$		2035sh, 2015br,s, 1846sh, 1830br,s
$Co_2(CO)_8$	2 $(C_5H_4Me)_3Sm$	2025vs, 1941br,s, 1841br,s, 1781br,s
$Co_2(CO)_8$	$AlBr_3$ [a]	2073s, 2064sh, 2047s, 2028s, 2023sh, 1864m, 1859m
(*b*) CH_2Cl_2 solutions		
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ [b]		2005s, 1958s, 1786s
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$	2 $(C_5H_4Me)_3Sm$	1993s, 1952m, 1772s, 1700w
$[(\pi\text{-}C_5H_5)Ni(CO)_2Fe(\pi\text{-}C_5H_5)(CO)$		1995s, 1810s
$[(\pi\text{-}C_5H_5)Ni(CO)_2Fe(\pi\text{-}C_5H_5)(CO)$	>2 $(C_5H_4Me)_3Ho$	2010s, 1738s
$[(\pi\text{-}C_5H_5)Ni(CO)_2Fe(\pi\text{-}C_5H_5)(CO)$	>2 $(C_5H_4Me)_3Gd$	2010s, 1738s
$[(\pi\text{-}C_5H_5)Ni(CO)]_2$		1886w, 1842s
$[(\pi\text{-}C_5H_5)Ni(CO)]_2$	$(C_5H_4Me)_3Er$	1888m, 1842br,s, 1780m
$[(\pi\text{-}C_5H_5)Ni(CO)]_2$	2 $(C_5H_4Me)_3Sm$	1888m, 1842br,s, 1780m
$(\pi\text{-}C_5H_5Me)Mn(CO)_3$		2018s, 1928br,s
$(\pi\text{-}C_5H_5Me)Mn(CO)_3$	1 or 2 $(C_5H_4Me)_3Sm$	2018s, 1928br,s, 1868m
$(\pi\text{-}C_5H_5Me)Mn(CO)_3$	$(cp)_3Er$ or $(cp)_3Yb$	2018s, 1928br,s, 1868m
$(\pi\text{-}C_5H_5Me)Mn(CO)_3$	>2 $(C_5H_4Me)_3Nd$	2018s, 1928br,s, 1865m
$(\pi\text{-}C_5H_5Me)Mn(CO)_3$	$(cp)_2YbCl$	2018s, 1928br,s
$(\pi\text{-}C_5H_5)Cr(NO)_2Cl$		1818s, 1712s
$(\pi\text{-}C_5H_5)Cr(NO)_2Cl$	>2 $(MeC_5H_4)_3Sm$	1818sh, 1775s, 1712sh, 1676s
$(\pi\text{-}C_5H_5)Cr(NO)_2Cl$	$(cp)_3Er$	1786s, 1688s
$(\pi\text{-}C_5H_5)Cr(NO)_2Cl$	$(cp)_3Yb$	1786s, 1686s
$(\pi\text{-}C_5H_5)Cr(NO)_2Cl$	$(cp)_2YbCl$	1818s, 1712s
$(\pi\text{-}C_5H_5)Cr(NO)_2Cl$	$(MeC_5H_4)_2YbCl$	1818s, 1784sh, 1712s, 1684sh
$(\pi\text{-}C_5H_5)Cr(CO)_2(NO)$		2018s, 1945s, 1692s
$(\pi\text{-}C_5H_5)Cr(CO)_2(NO)$	$(MeC_5H_4)_3Sm$	2038s, 2018s, 1973s, 1945s, 1692s, 1635s
$(\pi\text{-}C_5H_5)Cr(CO)_2(NO)$	$(MeC_5H_4)_3Ho$	2038s, 2018s, 1973s, 1945s, 1692s, 1635s
$(\pi\text{-}C_5H_5)Cr(CO)_2(NO)$	>2 $(MeC_5H_4)_3Ho$	2038s, 2018s, 1973s, 1945s, 1692s, 1635s
$(\pi\text{-}C_5H_5)Mo(CO)_2(NO)$		2016s, 1938s, 1662s
$(\pi\text{-}C_5H_5)Mo(CO)_2(NO)$	Up to 3 $(cp)_3Yb$	2035s, 2016s, 1968s, 1938s, 1662s, 1586s
$(\pi\text{-}C_5H_5)W(CO)_2(NO)$		2000s, 1923s, 1658s
$(\pi\text{-}C_5H_5)W(CO)_2(NO)$	$(MeC_5H_4)_3Er$	2030s, 2000s, 1955s, 1923s, 1658s, 1580s
$[(\pi\text{-}C_5H_5)Mn(CO)(NO)]_2$		1962s, 1785s, 1708s, 1510s
$[(\pi\text{-}C_5H_5)Mn(CO)(NO)]_2$	2 $(cp)_3Er$	1985br,s, 1790m, 1734s, 1708s, 1680s, 1525s
$[(\pi\text{-}C_5H_5)Mn(CO)(NO)]_2$	3 $(cp)_3Dy$	1990s, 1790m, 1735s, 1685s, 1525s
$[\pi\text{-}C_5H_5)Mn(CO)(NO)]_2$	4 $(cp)_3Er$	1990s, 1790vw, 1735s, 1685s, 1525s
(*c*) C_6H_6 solutions		
$(\pi\text{-}C_5H_5)Cr(NO)_2Cl$		1820s, 1705s
$(\pi\text{-}C_5H_5)Cr(NO)_2Cl$	$(MeC_5H_4)_3Sm$	1820m, 1775s, 1705m, 1680s

[a] Ref. 21. [b] Ref. 14.

The compounds $(\pi\text{-}C_5H_5)M(CO)_2(NO)$ [M = Cr, Mo, or W] possess both terminal nitrosyl and carbonyl ligands. Our spectral data indicate that the nitrosyl ligand in these complexes is a better Lewis base than the carbonyl ligands irrespective of the Group VI metal or lanthanide involved. For example, $(\pi\text{-}C_5H_5)Cr(CO)_2(NO)$, in the presence of an equimolar amount of $(C_5H_4Me)_3Sm$, exhibits new absorptions at 2038, 1973, and 1635 cm^{-1} in addition to those normally observed for the parent compound. The lowest band in this region of the i.r. spectrum clearly verifies the existence of an isonitrosyl linkage. The observed weakening of the N–O bond may be viewed as being caused by the withdrawal of electron density from the oxygen atom by the samarium and the resultant increase in the extent of back donation of electrons by the chromium atom into the π^* orbitals of the NO ligand. Since the $-NOSm(C_5H_4Me)_3$ group is thus a stronger π-acceptor than the terminal CO ligands,

---

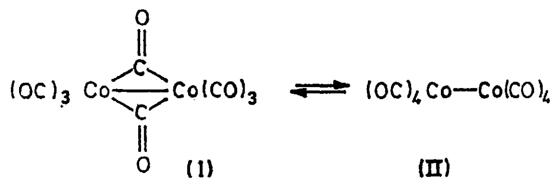
[13] F. A. Cotton, A. D. Liehr, and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1955, **1**, 175.

the Cr–CO π bonding in the adduct is reduced, thereby leading to a strengthening of the C–O bonds. Consequently, the two higher frequency carbonyl absorptions are observed. Again, an increase in the relative amount of R_3Ln beyond the 1 : 1 stoicheiometry does not cause complete complexation with any of the Group VI compounds, and all the adducts detected are exclusively of the isonitrosyl type.

(b) *Bridging Carbonyl Ligands.*—When $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ and $(C_5H_4Me)_3Sm$ are reacted in a 1 : 2 ratio in benzene at room temperature, a bright red air-sensitive solid rapidly precipitates. The elemental analyses of the recrystallized solid are consistent with the complex being formulated as $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2,2Sm(C_5H_4Me)_3$. The i.r. spectrum of this solid as a Nujol mull indicates that isocarbonyl linkages have been formed by the samarium atoms at each of the bridging carbonyl groups. The shift to higher frequencies of the terminal CO stretches and the shift to lower frequency of the bridging CO stretch relative to those observed for the parent iron compound are spectral features also exhibited by the known $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2,2AlEt_3$.[14] These shifts are again smaller in magnitude for the samarium complex than for the aluminium compound, but they do indicate that the two adducts are quite probably isostructural. An *X*-ray study [14] of the $AlEt_3$ adduct has conclusively shown the acidic aluminium atoms to be co-ordinated to the oxygen ends of the bridging carbonyl groups.

In donor or polar solvents, $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2,2Sm(C_5H_4Me)_3$ is almost completely dissociated. If $(\pi\text{-}C_5H_5)Ni(CO)_2Fe(\pi\text{-}C_5H_5)(CO)$ is employed as the Lewis base, however, only bridging isocarbonyl behaviour is observed for CH_2Cl_2 solutions containing greater than a twofold excess of R_3Ln. The mixed nickel–iron complex thus forms adducts which are less susceptible to dissociation and appears to be a better donor of electrons than the isoelectronic iron compound.

The molecular structure of dicobalt octacarbonyl in the solid state [15] is such that the two cobalt atoms and the two bridging CO groups are not in the same plane, the molecule having only C_s symmetry. In solution, however, $Co_2(CO)_8$ exists in two isomeric forms which are related by a temperature dependent equilibrium.[16–17] One isomer (I) corresponds to the crystalline substance whereas the other (II) has no bridging CO groups but only a cobalt–cobalt bond, *i.e.*



(I) (II)

One of the earliest reported examples of a Lewis acid complex with a carbonyl compound is $Co_2(CO)_8,AlBr_3$.[19] Although a single crystal *X*-ray study of this adduct has not yet been carried out, it is believed that the $AlBr_3$ is co-ordinated *via* a three-centre, two-electron bond to the formally bent cobalt–cobalt bond of isomer (I). Support for this structural proposal is the observation [20] that the i.r. spectrum (obtained with high resolution optics) of the adduct is virtually identical to that of the parent carbonyl in the CO-stretching region.* This result in itself is surprising since reasoning of the type outlined previously leads one to expect that the carbonyl stretches of the adduct should occur at a somewhat higher frequency. Interestingly, attempts to prepare the analogous complex with $AlEt_3$ lead only to a dark sludge devoid of carbonyl absorptions in the i.r. spectrum.[21]

When $Co_2(CO)_8$ and $(C_5H_4Me)_3Sm$ are reacted in a 1 : 1 ratio in toluene at room temperature, only a 1 : 2 adduct readily precipitates as an extremely air- and moisture-sensitive yellow solid. Its low resolution i.r. spectrum (as a Nujol mull) is qualitatively different from that reported for the $AlBr_3$ adduct, and it again exhibits the bands characteristic of bridging isocarbonyl linkages. Clearly, the presence of $(C_5H_4Me)_3Sm$ displaces the $Co_2(CO)_8$ equilibrium completely towards the form involving bridging CO ligands, the preferred sites of Lewis basicity. The $>CO\text{–}Sm(C_5H_4Me)_3$ bonds are established presumably because the hard lanthanide acid favours the harder oxygen of the CO groups over the softer metal–metal bond, although steric factors may also be operative during the formation of this novel compound. Regrettably, the adduct is not amenable to study in solution since it rapidly dissociates in those solvents in which it is soluble.

Like $Co_2(CO)_8$, the structurally-similar $[(\pi\text{-}C_5H_5)Ni(CO)]_2$ offers a number of sites capable of providing electrons for an appropriate acceptor. In solution the compound is believed to possess bridging carbonyl groups which are not coplanar with the two nickel atoms and a formally bent metal–metal bond.[22] When $[(\pi\text{-}C_5H_5)Ni(CO)]_2$ is treated with various R_3Ln complexes, a new band appears in the i.r. spectra at 1780 cm^{-1} and the band at *ca.* 1886 cm^{-1} becomes slightly more intense. These spectral features are characteristic of the formation of a 1 : 1 adduct,[21] and they confirm the preference of the lanthanides for the bridging carbonyl groups. The spectra are invariant when the lanthanide concentration is increased beyond the 1 : 1 stoicheiometry and thus there is no evidence of 1 : 2 adduct formation. Attempts to isolate the adducts from toluene solutions meet with failure.

The molecular structure of $[(\pi\text{-}C_5H_5)Mn(CO)(NO)]_2$ in

---

* *Note added in proof:* Recent re-investigations of this adduct revealed isocarbonyl bands *ca.* 1600 cm^{-1}, and higher terminal carbonyl stretching frequencies. See J. S. Kristoff, N. J. Nelson, and D. F. Shriver, *J. Organometallic Chem.*, 1973, **49**, C82 and G. Schmid and V. Bätzel, *ibid.*, 1972, **46**, 149.[4]

[14] N. J. Nelson, N. E. Kime, and D. F. Shriver, *J. Amer. Chem. Soc.*, 1969, **91**, 5173.

[15] G. G. Sumner, H. P. Klug, and L. E. Alexander, *Acta Cryst.*, 1964, **17**, 732.

[16] K. Noack, *Spectrochim. Acta*, 1963, **19**, 1925.

[17] G. Bor, *Spectrochim. Acta*, 1963, **19**, 2065.

[18] G. Bor and L. Markó, *Chem. and Ind.*, 1963, 912.

[19] P. Chini and R. Ercoli, *Gazzetta*, 1958, **88**, 1170.

[20] F. A. Cotton and R. R. Monchamp, *J. Chem. Soc.*, 1960, 1882.

[21] A. Alich, N. J. Nelson, D. Strope, and D. F. Shriver, *Inorg. Chem.*, 1972, **11**, 2976.

[22] J. F. Tilney-Bassett, *J. Chem. Soc.*, 1961, 577.

the solid state is not yet known with certainty.[23] In solution the compound is thought to exist as a mixture of dissymmetric *cis* and *trans* isomers, and recent ^1H n.m.r. studies[24] indicate that rapid intramolecular positional exchange of CO and NO groups occurs. The CH_2Cl_2 solution i.r. spectrum of the compound exhibits bands at 1962s [terminal ν(CO)], 1785s [bridging ν(CO)], 1708s [terminal ν(NO)], and 1510s cm^{-1} [bridging ν(NO)]. As progressively increasing amounts of R_3Ln species are added to this solution, new bands appear and intensify in the i.r. spectrum while the absorptions due to the parent carbonylnitrosyl gradually diminish in intensity. The limiting case is reached (Table 1) at a mole ratio of base : acid = 1 : 4 when the following bands are observed: 1990s, 1790vw, 1735s, 1680s, and 1525s cm^{-1}. This spectrum indicates that with $[(\pi\text{-}C_5H_5)Mn(CO)(NO)]_2$ bridging isocarbonyl and terminal isonitrosyl bonds have been preferentially formed by the lanthanide element. This result is unexpected since, arguing by analogy with the purely carbonyl systems, one would have predicted the Lewis acid to co-ordinate to the bridging nitrosyl ligand rather than the terminal one.

Not all carbonyl or nitrosyl ligands are sufficiently basic to form isocarbonyl or isonitrosyl linkages (as detected by i.r. spectroscopy) with the acids under investigation. For example, $Fe(CO)_2(NO)_2$, $(Ph_2MeP)_2Fe(NO)_2$, $(Me_2NCS_2)_2Fe(NO)$, $(\pi\text{-}C_5H_5)Fe(CO)_2I$, $(h^4\text{-}C_8H_8)Fe(CO)_3$, $(Ph_3P)_2Ru(NO)Cl_3$, and $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ exhibit no changes in their customary carbonyl and/or nitrosyl stretching frequencies when in solutions also containing various R_3Ln complexes. The $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ compound is particularly interesting because in the solid state it has a centrosymmetric molecular structure with a metal–metal bond and six terminal carbonyl ligands,[25] and this structure is believed to persist in solution.[26,27] Recently, Cotton[28] utilized ^{13}C n.m.r. while investigating the possibility of carbonyl transfer in the complex *via* a bridging intermediate. His study did not reveal any evidence for such an occurrence and our fruitless attempts to detect or trap any bridged intermediate with the lanthanide acids also suggest that this mechanism is inoperative for the parent carbonyl compound. Moreover, the lanthanides are apparently not sufficiently acidic to induce a bridged–nonbridged equilibrium in solution. A recent report by Shriver,[21] however, indicates that $Al(Pr^i)_3$ in heptane (at concentrations that are unattainable for the R_3Ln complexes) forms an equilibrium product with $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ which displays the behaviour expected for an adduct stabilized by two AlR_3-co-ordinated bridging carbonyls.

(c) *Other Base Sites.*—The interaction of the R_3Ln complexes with Lewis bases can also be monitored by ^1H n.m.r. spectroscopy as shown by the representative data displayed in Table 2. This physical technique is not hampered by the presence of an excess of Lewis base and, furthermore, it is quite sensitive, even detecting adduct formation for some complexes, *e.g.* $(h^4\text{-}C_8H_8)Fe(CO)_3$, whose i.r. spectra do not change in the presence of R_3Ln. It cannot, however, independently provide information about which base site is being utilized in a compound possessing a number of such sites. For several compounds such a distinction does not have to be made. Thus, for example, the ^1H n.m.r. spectrum of $(\pi\text{-}C_5H_5)_2WH_2$ in a benzene solution also containing $(C_5H_4Me)_3Nd$ [particularly chosen because it does not appreciably broaden the observed resonances] shows upfield shifts of both the cyclopentadienyl and hydride resonances. This effect can readily be ascribed to a paramagnetic shift of the signals resulting from a Lewis adduct in which the lone pair of electrons situated on tungsten forms a co-ordinate bond to neodymium. Similar compounds are known[29-31] in which R_3Al functions as the electron acceptor.

TABLE 2

Changes induced by $(C_5H_4Me)_3Nd$ in the ^1H n.m.r. spectra of various Lewis bases

Lewis base	Concentration/ M	τ,[a] p.p.m.	Upfield shift,[b] p.p.m.
$(\pi\text{-}C_5H_4Me)Mn(CO)_3$	10^{-1}	5·74;[c] 8·34[d]	0·36;[c] 0·26[d]
$(\pi\text{-}C_5H_5)Cr(CO)_2(NO)$	10^{-1}	5·67	1·76
$h^4\text{-}C_8H_8Fe(CO)_3$	10^{-1}	5·14	0·28
$[(\pi\text{-}C_5H_5)Ni(CO)]_2$	10^{-1}	4·78	1·10
$(\pi\text{-}C_5H_5)Fe(CO)_2I$	10^{-1}	5·96	1·09
$(\pi\text{-}C_5H_5)_2WH_2$	10^{-1}	5·68;[c] 23·2[e]	0·36;[c] 2·3[e]
$C_6H_5C{\equiv}CH$	10^{0}	7·20[f]	0·11[f]

All samples, except the one involving $C_6H_5C{\equiv}CH$, were prepared with a saturated benzene solution of $(C_5H_4Me)_3Nd$ such that the molar ratio of neodymium : base was 1 : 2.

[a] Spectrum of pure compound relative to TMS (τ = 10). [b] Shift in resonances after adding $(C_5H_4Me)_3Nd$. [c] Cyclopentadienyl protons. [d] Methyl protons. [e] Hydride protons. [f] Acetylenic proton.

The observation that $(C_5H_4Me)_3Nd$ induces an upfield shift in the acetylenic proton resonance of phenylacetylene is quite interesting in that Tsutsui[32] has reported that R_3Sm catalyses the trimerization of the alkyne to 1,3,5-triphenylbenzene. Our result substantiates the role of the lanthanide element as a co-ordination site for π-bases in such process. Further, the $(\pi\text{-}C_5H_5)Fe(CO)_2X$ [X = Cl or I] compounds react with $(C_5H_4Me)_3Nd$ in benzene, although the iodide does so sufficiently slowly for an n.m.r. spectrum of the solution to be recorded. This spectrum shows an upfield shift of the cyclopentadienyl ^1H resonance. Co-ordination of the Lewis acid can, in principle, occur at either the CO or I ligand, but

---

[23] B. F. G. Johnson and J. A. McCleverty, *Progr. Inorg. Chem.*, 1966, **7**, 277.

[24] T. J. Marks and J. S. Kristoff, *J. Organometallic Chem.*, 1972, **42**, C91.

[25] F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, 1957, **27**, 809.

[26] P. Braterman and D. Thompson, *J. Chem. Soc. (A)*, 1968, 1454.

[27] R. D. Fischer and K. Noack, *J. Organometallic Chem.*, 1969, **16**, 125.

[28] R. D. Adams and F. A. Cotton, *J. Amer. Chem. Soc.*, 1972, **94**, 6193.

[29] A. Storr and B. S. Thomas, *Canad. J. Chem.*, 1971, **49**, 2504.

[30] J. C. Kotz and D. G. Pedrotty, *Organometallic Chem. Rev. A*, 1969, **4**, 479.

[31] D. F. Shriver, *Accounts Chem. Res.*, 1970, **3**, 231.

[32] H. Gysling and M. Tsutsui, *Adv. Organometallic Chem.*, 1970, **9**, 361.

in view of our i.r. results, we believe that the neodymium is probably attached at the halide site.

Marks *et al.*[4] have shown that Eu(fod)$_3$ [fod = a substituted β-diketonate] can be used to shift the ^{1}H n.m.r. signals of appropriate compounds since it also co-ordinates at a variety of base sites including carbonyl ligands. A direct comparison of the Eu(fod)$_3$ and $(C_5H_4Me)_3Nd$ shift reagents as chemical and structural probes is not possible because of the different conditions existing in both sets of experiments. We would emphasize, however, that in spite of the substantial shifts induced by $(C_5H_4Me)_3Nd$ (Table 2), it is not suitable for general use as a shift reagent because of (a) its low solubility in common organic solvents, (b) its sensitivity to air and moisture, (c) its noticeable decomposition in chlorinated or acidic solvents, and (d) its reactivity with some substrates of interest. [A good illustration of the latter handicap is the fact that $(C_5H_4Me)_3Ne$ reacts rapidly with $(\pi\text{-}C_5H_5)_2Sn$ in benzene to yield a precipitate which leaves the supernatant solution devoid of ^{1}H resonances. The precipitate appears to be the product of an oxidation–reduction reaction, and its exact nature is being investigated further.] The corresponding R$_3$Eu compound is very difficult to desolvate reproducibly, although it does produce large downfield shifts for the ^{1}H resonances of a number of bases.[33] Nevertheless, $(C_5H_4Me)_3Nd$ can be employed to detect solution interactions which are difficult to determine otherwise, and the interactions with the stronger bases do appear to produce the larger shifts.

TABLE 3

Infrared spectra of $R_2LnM(\pi\text{-}C_5H_5)(CO)_3$ species

Compound	ν(CO)/cm^{-1}	Other absorptions/cm^{-1}
$(cp)_2YbW(\pi\text{-}C_5H_5)(CO)_3$		
in THF	2010m, 1936s, 1890s, 1790s, 1740s	
as Nujol mull	2010m, 1984s, 1934s, 1890br,s, 1790br,s, 1565br,s	1045m, 1012m, 892w, 790m, 662w, 584m, 505m, 484m
$(MeC_5H_4)_2HoW(\pi\text{-}C_5H_5)(CO)_3$		
in THF	2010m, 1936s, 1890s, 1790s, 1740s	
as Nujol mull	2010m, 1976s, 1930br,s, 1880br,s, 1750br,s, 1560br,s	1040m, 1010m, 780ms, 580m, 505m, 484m
$(cp)_2DyW(\pi\text{-}C_5H_5)(CO)_3$		
as Nujol mull	2010m, 1980s, 1934br,s, 1890br,s, 1770br,s, 1570br,s	1045w, 1012ms, 890w, 780ms, 690ms, 662mw, 580m, 505m, 484m
$(cp)_2ErW(\pi\text{-}C_5H_5)(CO)_3$		
as Nujol mull	2010m, 1980m, 1910br,s, 1780br,s, 1560br,s	
$(cp)_2ErMo(\pi\text{-}C_5H_5)(CO)_3$		
as Nujol mull	2020m, 1940s, 1885br,s, 1770br,s, 1690br,s	1045w, 1010m, 780m, 505w
$Er[(\pi\text{-}C_5H_5)Mo(CO)_3]_3,7H_2O$		
as Nujol mull	2020s, 1982s, 1940br,s, 1780br,w, 1690br,w	3600—3400br,m, 1010w, 810ms, 655m, 580m, 570m, 515w, 485m, 455w
$Na[(\pi\text{-}C_5H_5)W(CO)_3]$		
in THF	1936m, 1892br,s, 1790s, 1740s	
as Nujol mull	1980s, 1890s, 1772s, 1690s	805m, 585m, 515m, 505m
$Na[(\pi\text{-}C_5H_5)Mo(CO)_3]$		
in THF	1940m, 1895s, 1790s, 1740s	
as Nujol mull	1940w, 1895s, 1775s, 1690s	

Reactions involving Metal Carbonyl Anions.—The ^{1}H n.m.r. evidence for the existence of a tungsten–neodymium bond in benzene solutions containing $(\pi\text{-}C_5H_5)_2WH_2$ and $(C_5H_4Me)_3Nd$ prompted us to investigate the products of the reactions between R$_2$LnCl compounds and various metal carbonyl anions. Two types of lanthanide-containing complexes could possibly result from such reactions. The first class would contain a transition metal–lanthanide bond such as the one believed to occur in the unique compound $Er[Co(CO)_4]_3,3C_4H_8O$ which is prepared from $Hg[Co(CO)_4]_2$ and a 1% *w/w* Er/Hg mixture.[34] The second class would involve co-ordination of the lanthanide to the carbonyl fragment *via* an isocarbonyl linkage of the type reported[13] for $[Ph_3Al\text{-}W(CO)_3(\pi\text{-}C_5H_5)]^-[NBu^n_4]^+$, which is simply prepared by mixing equimolar amounts of Ph$_3$Al and $[(\pi\text{-}C_5H_5)\text{-}W(CO)_3]^-[NBu^n_4]^+$ in dichloromethane.

When R$_2$LnCl and $Na[(\pi\text{-}C_5H_5)W(CO)_3]$ are reacted in a 1 : 1 ratio in THF, the analytically pure $R_2LnW(\pi\text{-}C_5H_5)(CO)_3$ [Ln = Dy, Ho, Er, or Yb] complexes can be isolated in good yields. Other carbonyl anions, however, do not produce analogous derivatives. For example, $[Co(CO)_4]^-$ is not sufficiently nucleophilic[35] to react with the organolanthanide compound, while $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ and $[(\pi\text{-}C_5H_5)Mo(CO)_3]^-$ result in the contamination of the products with their corresponding neutral dimers.

The lanthanide–tungsten compounds are obtained as solvent-free crystals which are thermally stable up to 220 °C, soluble only in strongly donor solvents such as

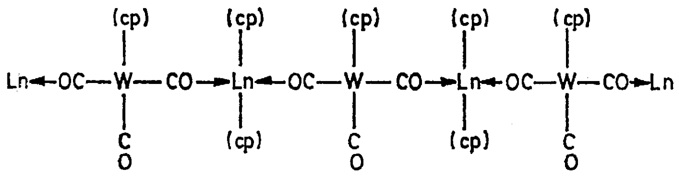
---

[33] A. E. Crease and P. Legzdins, unpublished results.

[34] R. S. Marianelli and M. T. Durney, *J. Organometallic Chem.*, 1971, **32**, C41.

[35] A. J. Cleland, S. A. Fieldhouse, B. H. Freeland, and R. J. O'Brien, *Chem. Comm.*, 1971, 155; R. E. Dessy, R. B. King, and R. L. Pohl, *J. Amer. Chem. Soc.*, 1966, **88**, 5121.

THF and DMSO, and decomposed by various halogenated solvents. Their i.r. spectra in THF solutions (Table 3) show strong bands which are identical to those exhibited by the free carbonyl anion, thereby suggesting substantial dissociation of the compounds. A comparison of the mull spectra of $R_2LnW(\pi\text{-}C_5H_5)(CO)_3$ and $Na[(\pi\text{-}C_5H_5)W(CO)_3]$, however, reveals that the former complexes exhibit additional bands at *ca.* 2010m and *ca.* 1940s cm^{-1} as well as a lowering of the lowest carbonyl stretching frequency to *ca.* 1565 cm^{-1}. These features can be interpreted as indicating the formation of some isocarbonyl bonds, and the large number of CO-stretching absorptions suggests a polymeric structure for these compounds. The existence of bridging carbonyl groups in this structure seems unlikely in view of the covalent radii of the metals involved. Moreover, such bridges would involve lanthanide–carbon *sigma*-bonds which would have to cleave in solution. Generally, lanthanide compounds thought to involve such σ-bonds, with the notable exception of $Lu(C_8H_9)_4^-$,[36] are very insoluble polymeric materials which are difficult to obtain in a pure state.[6] A structure which is consistent with the experimental observations is one in which the tungsten units are linked *via* a bridging framework of the type shown below:



$$\mathrm{Ln\leftarrow OC-\overset{(cp)}{\underset{CO}{W}}-CO\rightarrow\overset{(cp)}{\underset{(cp)}{Ln}}\leftarrow OC-\overset{(cp)}{\underset{CO}{W}}-CO\rightarrow\overset{(cp)}{\underset{(cp)}{Ln}}\leftarrow OC-\overset{(cp)}{\underset{CO}{W}}-CO\rightarrow Ln}$$

Such an arrangement satisfies the requirement that there be one or more isocarbonyls and one or more terminal carbonyls present.

Unlike $Na[(\pi\text{-}C_5H_5)W(CO)_3]$ which rapidly smoulders in air,* the $R_2LnW(\pi\text{-}C_5H_5)(CO)_3$ salts turn deep red in dry air over a period of two days. Sublimation of this red solid yields pure $[(\pi\text{-}C_5H_5)W(CO)_3]_2$ which can be identified by its elemental analysis, m.p., and i.r. spectrum. Indeed, attempts to prepare the $R_2LnMo(\pi\text{-}C_5H_5)(CO)_3$ analogues always yield some $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ just because the former complexes are extremely sensitive to oxidation. Wilkinson[37] has shown that $(\pi\text{-}C_5H_5)Mo(CO)_3H$ also oxidizes in air to the dimer. This similarity in behaviour of the anion and the hydride suggests that it should be possible to nitrosylate the anion directly, thereby eliminating the intermediate conversion of the anion to the hydride during the preparation of $(\pi\text{-}C_5H_5)M(CO)_2(NO)$[38] [M = Cr, Mo, or W]. We find, in fact, that good yields (>60% based on the anion) of the desired nitrosyls are obtained if the metal carbonyl anions are treated in diethyl ether with *N*-methyl-*N*-nitroso-*p*-toluenesulphonamide. Only one other instance is known[39] in which this nitrosylating agent converts a carbonyl anion to a nitrosyl, *i.e.* $[Mn(CO)_5]^-$ to $Mn(CO)_4(NO)$, and we are presently investigating the general utility of this reagent during the synthesis of new metal nitrosyls.

Clearly the $Na[(\pi\text{-}C_5H_5)M(CO)_3]$ and $R_2LnM(\pi\text{-}C_5H_5)(CO)_3$ salts possess similar chemical properties. We have already noted the oxidation of both species to the neutral carbonyl dimers. In addition, the lanthanide complexes can also be nitrosylated in THF with *N*-methyl-*N*-nitroso-*p*-toluenesulphonamide to produce $(\pi\text{-}C_5H_5)M(CO)_2(NO)$. This analogous behaviour suggests that another synthetic route to the $R_2LnM(\pi\text{-}C_5H_5)(CO)_2$ complexes might be

$$R_3Ln + M(CO)_6 \xrightarrow[\text{reflux}]{\text{THF}} R_2LnM(\pi\text{-}C_5H_5)(CO)_3 + CO$$
$$R = C_5H_5 \text{ or } C_5H_4Me;\ M = Cr, Mo, \text{ or } W \qquad (A)$$

This route is of interest because R_2LnCl compounds only exist for lanthanides heavier than neodymium, and hence the previously described method of preparing (A) is not accessible for all the rare earths. Of the Group VI carbonyls only $Mo(CO)_6$ reacts with the R_3Ln compounds under the conditions studied. Gas is evolved as expected and products can be isolated for Ln = La, Er, and Ho. The analytical data of these products reveal the presence of some $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$, but the mull i.r. spectra exhibit the characteristic isocarbonyl absorptions also observed for the tungsten analogues.

Finally, we have also attempted to prepare the totally substituted derivatives LnA_3 [A = metal carbonyl anion] from the metathetical reactions

$$LnCl_3 + 3\,NaA \xrightarrow{H_2O} LnA_3 + 3\,NaCl$$

A number of carbonyl anions react readily in the expected manner, but in all cases the products formed are intractable air-sensitive solids which are totally insoluble in water or common organic solvents and do not sublime. We are reporting only one such complex, namely $Er[(\pi\text{-}C_5H_5)Mo(CO)_3]_3,7H_2O$, which we believe to be reasonably pure. The i.r. spectrum of this complex verifies the presence of water and shows strong terminal CO bands and only weak lower frequency CO bands. It thus appears that $Er[(\pi\text{-}C_5H_5)Mo(CO)_3]_3,7H_2O$ is somewhat similar to $Er[Co(CO)_4]_3,3THF$[34] in that there may be some metal–metal bonding made possible by the substantial solvation of the electropositive lanthanide element.

We gratefully acknowledge the support of this work by the Research Corporation in the form of a Frederick Gardner Cottrell grant to P. L. and by the National Research Council of Canada in the form of a predoctoral fellowship to A. E. C.

[3/071 *Received, 12th January, 1973*]

---

* Controlled air oxidation of $Na[(\pi\text{-}C_5H_5)W(CO)_3]$ yields some $[(\pi\text{-}C_5H_5)W(CO)_3]_2$.

[36] S. A. Cotton, F. A. Hart, M. B. Hursthouse, and A. J. Welch, *J.C.S. Chem. Comm.*, 1972, 1225.

[37] T. S. Piper and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **3**, 104.

[38] R. B. King and M. B. Bisnette, *Inorg. Chem.*, 1967, **6**, 469.

[39] T. H. Coffield, U.S.P. 2,967,087.