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Preliminary communication

Rare earth shift reagents as chemical and structural probes for organometallic compounds

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Recent work[1] has shown that lanthanide nuclear magnetic resonance 'shift reagents' are structural tools of great utility in organic chemistry. We report here that many ligands and some metals possess sufficient basicity to interact with the shift reagent $Eu(fod)_3$[1c ★]. As a result, the lanthanide shift reagents should prove useful in NMR studies of many organometallic and coordination compounds, as spectral, structural, and chemical probes.

Compounds containing halides and pseudohalides such as F, Cl, N_3, and CN were observed to interact with $Eu(fod)_3$ while those containing Br, I and NCS did not give observable shifts under the conditions of our experiments (Table 1). In the case of solutions containing $(h^5\text{-}C_5H_5)Fe(CO)_2CN$, the equilibrium mixture of bridged and nonbridged species was observed and the identity of the donor site, CN, was verified by the characteristic increase in $\nu(CN)$. The data for $(h^5\text{-}C_5H_5)Mo(CO)_3Ge(X)(C_6H_5)_2$ where X = F, Cl indicate that fluoride coordinates preferentially to europium. These observations as well as others in this communication demonstrate that the europium shift reagent is a hard Lewis acid, which is in harmony with general lanthanide chemistry.

The lack of observed shift for $(h^5\text{-}C_5H_5)Fe(CO)_2CH_3$ when contrasted with the observed shift for $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$ indicates that bridging metal carbonyl groups are more basic than terminal groups, in accord with previous results[2]. However, the dipolar shifts observed for $(phen)[(C_6H_5)_3P]_2Mo(CO)_2$ are in accord with the notion that terminal carbonyls with sufficiently low CO stretching frequencies may serve as Lewis bases[3]. These results provide the first evidence for a metal other than aluminum interacting with a coordinated carbonyl. The basicity of $M\text{-}SO_2CH_3$ with H^+ and BF_3, and of $M\text{-}COCH_3$ complexes with H^+ is known[4,5], however, the present work yields the first indication that a metal can interact with these coordinated ligands[★★].

Substantial shifts were also observed with the transition metal base, $(h^5\text{-}C_5H_5)_2WH_2$, and with the main group metal base, $(h^5\text{-}C_5H_5)_2Sn$. In both cases, addition of tetrahydrofuran displaced the metal base from the lanthanide complex and regenerated the unshifted PMR spectrum of the metal base. These systems provide the first evidence for transition metal–lanthanide and non-transition metal–lanthanide bonds.

[★] fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate.

[★★] In addition it has been recently shown that standard basic functional groups on organic ligands are susceptible to coordination by shift reagents, *cf.* ref. 6.

TABLE 1

OBSERVED SHIFTS FOR METAL COMPLEXES WITH Eu(fod)$_3$ [a]

Compound	Concentration (M)	Concentration Eu(fod)$_3$(M)	Max.recorded[b] shift of protons (ppm)	
(h^5-C_5H_5)$_2$Ti(N_3)$_2$	0.31	0.30		0.47
[(C_6H_5)$_3$P]$_2$Ir(CO)Cl	0.10	0.30	*ortho*	0.10
			meta,para	0
(h^5-C_5H_5)$_2$TiCl_2	0.16	0.34	C_5H_5	0.10
(C_6H_5)$_3$SnCl	0.33	0.24	*ortho*	0.03
			meta,para	0
[(CH_3)$_2$(C_6H_5)As]$_2$Ru(NO)Cl_3	0.26	0.27	CH_3	0.17
			ortho	0.07
			meta,para	0
(h^5-C_5H_5)Fe(CO)($COCH_3$)P(n-C_4H_9)$_3$	0.33	0.35	C_5H_5	3.62
			$COCH_3$	3.56
			α-CH_2	3.82
			β-CH_2	2.60
			γ-CH_2	0.50
			CH_3	0.27
(h^5-C_5H_5)Mo(CO)$_3$Ge(C_6H_5)$_2$F	0.33	0.17	C_5H_5	0.55
			ortho	1.03
			meta,para	0.07
(h^5-C_5H_5)Mo(CO)$_3$Ge(C_6H_5)$_2$Cl	0.16	0.30	C_5H_5	0
			ortho	0.03
			meta,para	0.01
(h^5-C_5H_5)Fe(CO)$_2$$CH_3$	0.33	0.23	CH_3	0
			C_5H_5	0
(h^5-C_5H_5)Fe(CO)$_2$CN	0.10	0.22	C_5H_5	3.81
(h^5-C_5H_5)Fe(CO)$_2$Cl	0.10	0.34	C_5H_5	3.12
(h^5-C_5H_5)Fe(CO)$_2$Br	0.10	0.19	C_5H_5	0
(h^5-C_5H_5)Fe(CO)$_2$I	0.10	0.15	C_5H_5	0
(h^5-C_5H_5)Fe(CO)$_2$NCS	0.10	0.07	C_5H_5	0
(h^5-C_5H_5)Fe(CO)$_2$(SO_2CH_3)	0.10	0.01	CH_3	0.87
			C_5H_5	0.53
[(h^5-C_5H_5)Fe(CO)$_2$]$_2$	0.032	0.12	C_5H_5	0.35
(phen)[P(C_6H_5)$_3$]$_2$Mo(CO)$_2$[c]	0.018	0.055	broad feature	0.27
			broad feature	0.48
(dmp)[P(C_6H_5)$_3$]$_2$Mo(CO)$_2$[c]	0.023	0.030		ca. 0.18
(h^5-C_5H_5)$_2$Sn	0.65	0.17		0.75
(h^5-C_5H_5)$_2$WH_2	0.19	0.14	C_5H_5	1.78
			H	-2.11

[a] Data were obtained at 60 MHz for complexes dissolved in toluene-d_8 or chloroform-d_1 with TMS as an internal reference. Maximum recorded shifts (not necessarily the limit at very high Eu(fod)$_3$ concentrations) are presented. [b] Positive entries represent downfield shifts. The estimated precision is ±0.025 ppm. [c] Decomposes fairly rapidly in $CDCl_3$ solution. phen = 1,10-phenanthroline; dmp = 5,6-dimethyl-1,10-phenanthroline.

The utility of the shift reagent in spectral simplification is illustrated in Table 1, which presents the result of adding Eu(fod)$_3$ to a toluene-d_8 solution of (h^5-C_5H_5)Fe($COCH_3$)(CO)P(C_4H_9)$_3$. Dipolar shifts considerably expand the PMR spectrum, while sharpness of the lines in the shifted spectrum permits detection of the spin–spin coupling between the phosphorus and cyclopentadienyl protons, indicating that the iron–phosphorus bond has remained intact. Of interest also is the observation that only certain multiplets in the phenyl PMR resonances of phenylarsine and -phosphine (*cis* to halogen) complexes are shifted upon addition of Eu(fod)$_3$. The spatial dependence of the dipolar shift[1] implies that these resonances are due to *ortho* protons on the phenyl rings. Thus the rare earth shift reagents offer considerable promise in inorganic and organometallic chemistry for spectral simplification and stereochemical mapping. Of perhaps equal importance is the application of shift reagents as a convenient tool for probing the basicity of metal complexes.

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