strongly favors the mechanisms in Scheme IV. Like **7** (−1.6 V/SCE), **6** must have a very negative oxidation potential implying fast electron transfer to O_2 (−0.7 V/SCE) as in the first step of Scheme IV.

Protonation of **2** by HPF_6 gives $\mathbf{1}^{2+}(PF_6^-)_2$ directly without isolation of the intermediate complex $[(C_6Me_6)(\eta^5\text{-}C_6Me_5CH_2)Fe]^+PF_6^-$ (**9**), which indicates that the methylene carbon is more basic in **9** than in **2**. This reaction gives a 50% yield from **1**, which provides an estimate of the reaction yield **1** → **2**. Reaction of **2** with PhCOCl gives the double benzoylation product **10** (Scheme V). Again the monobenzoylated intermediate cannot be isolated; intra- or intermolecular proton transfer from a benzoylated methylene to a nonbenzoylated one occurs, affording a second benzoylation of this alkylidene unit. ^1H and ^{13}C NMR data indicate 75% of enolic form in the β-diketone **10**.

In conclusion, entries to functionalized bis(arene)iron complexes are provided by C–H activation and C–C bond formation using electron-transfer reactions from the readily available complex **1** and the simple substrates RX and O_2.

Acknowledgment. We thank Professor F. Varret and Dr. J.-P. Mariot (Le Mans) for Mössbauer facilities and S. Sinbandhit, D. Catheline, P. Michaud, and D. Mandon (Rennes) for useful experimental assistance. This work was supported by the CNRS (ATP No. 9812).

Registry No. 1, 55280-55-2; $\mathbf{1}^+PF_6^-$, 53382-61-9; $\mathbf{1}^+,{}^1/_2O_2^{2-}$, 89278-40-0; $\mathbf{1}^{2+}(PF_6^-)_2$, 53382-63-1; **2**, 89278-41-1; **3a**, 89278-43-3; **3b**, 89278-45-5; **3c**, 89278-47-7; **3d**, 89278-49-9; **3e**, 89278-51-3; **7**, 89361-30-8; **8**, 89278-52-4; **10**, 89278-53-5.

Supplementary Material Available: ^1H and ^{13}C NMR, infrared, and analytical data for **3a–e**, **8**, and **10** (2 pages). Ordering information is given on any current masthead page.

Near-Infrared f-f Transition Cotton Effects of Ytterbium(III) Ion: Experimental Evidences for Interaction between Rifamycin Antibiotics and Metal Ions

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Received November 29, 1983

Lanthanide ions have been used for some time as paramagnetic[1] or fluorescent[2] probes to study the binding of metals to biological molecules. Near-infrared circular dichroism (near-IR-CD) associated with f–f electronic transitions of the above ions can also be exploited to obtain this kind of information. Indeed several lanthanide ions exhibit[3,4] magnetic dipole allowed transitions between 800 and 2000 nm, and intense CD bands are to be expected when the ion is perturbed by a chiral organic ligand. Only very weak CD bands of the latter, due to the overtones of vibrational excitations,[5] are present in the above spectral region. Therefore, the appearance of near-IR-CD bands is directly connected to the metal–ligand complex formation. Furthermore, as the observed CD is dependent on the crystal field around the metal, in principle, information about the structure of the metal–ligand adduct can be obtained by means of near-IR-CD measurements.

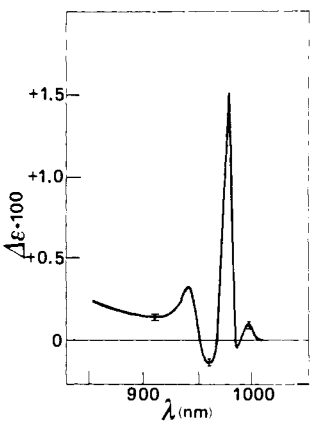
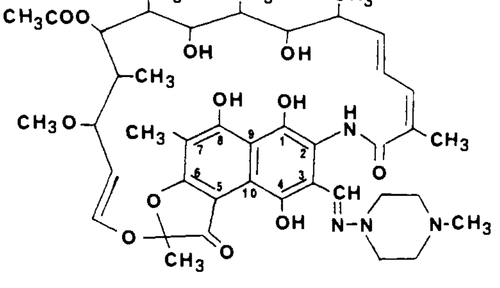


Figure 1. CD curve of **1**/Yb(III) adduct in MeOH/H_2O (98/2) solution at pH 5–6 [c(**1**) 2.7 mmol/L, c($YbCl_3$) 2 mmol/L]. Δε values in the figure have been arbitrarily referred to the overall Yb(III) concentration. The noise level is indicated by vertical error bars.

An interesting application is provided by the use of Yb(III) ions to probe the interaction between rifampicin (**1**) and physiologically important ions, like Ca(II), which lack appropriate spectroscopic characteristics for direct observation of their binding to biological molecules.[6] The Yb(III) ion exhibits[3,4] a magnetic dipole allowed transition, $^2F_{7/2} \rightarrow {}^2F_{5/2}$, at about 1000 nm, and its replacement of the Ca(II) ion may be considered as isomorphous, since the ionic radii are 0.94 and 0.99 Å, respectively.



1

The CD spectra of **1** in a pH 5–6 methanol/water (98/2) solution have been obtained[10] in the range 185–1200 nm both in the absence and in the presence of the metal ions, Ca(II) and Yb(III). The absorption and CD spectra in the UV-vis region are not reported here, as no remarkable variations are observed in this region, dominated by the exciton coupling of the ansadiene and naphthohydroquinone chromophores.[11] Slight differences may be due simply to different experimental conditions (pH, metal ion concentration, etc.). In Figure 1, the CD spectrum of **1** in the presence of Yb(III) ions is reported between 700 and 1100 nm. At least five oppositely signed bands can be observed in this region, the 974-nm component showing a high dissymmetry factor ($g \simeq 0.01$). The appearance of strong optically active bands, due to the crystal field splitting of the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ electronic transition

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[1] (a) Niboer, E. *Struct. Bonding (Berlin)* **1975**, *22*, 1. (b) Horrocks, W. D., Jr.; Sudnick D. R. *Acc. Chem. Res.* **1981**, *14*, 384.

[2] Richardson, F. S. *Chem Rev.* **1982**, *82*, 541.

[3] Stein, G.; Wurzberg, E. *J. Chem. Phys.* **1975**, *62*, 211.

[4] Peacock, R. D. *Struct. Bonding (Berlin)* **1975**, *22*, 83.

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[6] The mechanism of action of **1** seems to require[7,8] the inhibition of DNA-dependent RNA polymerase **2**, possibly via complexation of **1** with **2**, by means of the Zn(II) ion of **2**. Moreover it has been recently reported[9] that **1** can also be involved in the methabolism of Ca(II) ions.

[7] Weherli, W.; Stahelin, N. In "Antibiotics—III—Mechanism of antimicrobial and antitumor agents"; Corcoran, J. W., Hahn, F., Eds.; Springer-Verlag: West Berlin, 1975; pp 252–268.

[8] Scrutton, M. C.; Wu, C. W.; Goldtwait, D. A. *Proc. Natl. Acad. Sci. U.S.A.* **1971**, *68*, 2497.

[9] Araszkiecz, A.; Miravet, L.; Cohen-Solal, L.; Hioco, D. *C. R. Soc. Biol.* **1973**, *167*, 875.

[10] In the near-IR region the CD spectra were recorded with a JASCO J 200-D spectrometer, equipped with a DP-500 N data processor, by using standard cylindrical quartz cells. Methanol/water (98/2) solutions at pH 5–6, c(**1**) 2.7 mmol/L, c($YbCl_3$ or $CaCl_2$) 2 mmol/L, have been employed in the examined region. A constant spectral bandwidth of 3 nm was used thoroughout.

[11] Salvadori, P.; Bertucci, C.; Rosini, C.; Zandomeneghi, M.; Gallo G. G.; Martinelli, E.; Ferrari, P. *J. Am. Chem. Soc.* **1981**, *103*, 5553.

of Yb(III), is direct unambiguous evidence of interaction between the lanthanide ion and the antibiotic molecule. The number, energy spacings, and relative intensities of the bands can, in principle, give detailed information about the Yb(III) coordination site. Unfortunately, relationships between the near-IR–CD spectra and the structure of lanthanide complexes are not yet available, so well-defined structural information can not be obtained: however, even a qualitative analysis can offer some interesting suggestions.[12] According to a recent report,[13] strong lanthanide CD will be observable only when a chiral ligand is linked directly to the Ln(III) ion and there is some Ln(III)–ligand multidentate chelation. It is generally accepted that the preferred binding sites for the lanthanide ions will be those containing negatively charged groups (oxygen atoms, for instance); so it appears reasonable to assume that the acid function at the 8-position in **1** provides the strongest binding site. Experimental support for this hypothesis has been obtained by carrying out the measurement on the unionized form at pH $\simeq 2$ in the presence of Yb(III) ions. Under this condition there is no CD signal detectable between 1100 and 700 nm. Other donor groups that can promote the multidentate coordination enhancing the CD intensity are the hydroxyl groups in the ansa ring, which are directly linked to chiral centers. The remaining coordination positions of the ion may be reasonably assumed to be occupied by solvent molecules.

In conclusion, while further study has to be carried out on chiral Yb(III) compounds in order to relate the CD of f–f transitions and structure, the present communication shows that the above ions constitute a suitable probe for the interactions of "transparent" divalent alkaline-earth metal ions and biological molecules.

Acknowledgment. This investigation was partially supported by a grant from Ministero della Pubblica Istruzione, Roma.

Registry No. Rifampicin, 13292-46-1; Yb^{3+}, 18923-27-8.

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[13] Richardson, F. S.; Das Gupta, A. *J. Am. Chem. Soc.* **1981**, *103*, 5716.

Acyllithium to Lithium Enolate Conversion by a 1,2-Silicon Shift. A Shortcut to Acylsilane Enolates

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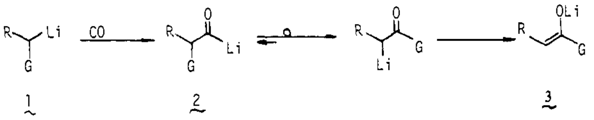
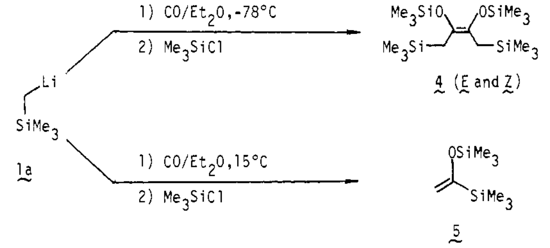
Received December 13, 1983

One of the key organic intermediates that heretofore has rarely been utilized in practical synthetic reactions is the negatively charged carbonyl species, carbonyl anion (acyl- or aroyllithium) **2**. They have long been suggested as the first intermediate in the reaction of organolithium **1** with carbon monoxide. The reactions are quite complex and give various products in a nonselective manner. Incorporation of at least two aryl or alkyl moieties into the products is usually inevitable.[1,2] However, Seyferth et al. have very recently succeeded in the efficient in situ trapping of acyllithium with electrophiles (Me$_3$SiCl[3a] or carbonyl compounds[3b–d], using extremely careful reaction conditions (a controlled, slow-rate addition of RLi at −110 °C). The commonly observed complex results of the reaction of alkyllithium with carbon monoxide could be attributed to the exceedingly reactive nature of acyllithium and alkyllithium, and, therefore, the development of a method for the immediate conversion of the highly reactive acyllithium to a more stable but still reactive synthetic intermediate seemed desirable. Thus, our strategy involves acyllithium to lithium enolate conversion.[4] We wish to report here the realization of this concept by utilizing the well-known 1,2-silicon shift[5] (eq 1, G = R$_3$Si).[6]



(1)

When silylmethyllithium **1a**[7] was exposed to carbon monoxide (1 atm) at −78 °C in ether, gradual absorption of carbon monoxide over a period of 2 h was observed. Quenching with Me$_3$SiCl gave an enediol disilyl ether **4** as a major product (eq 2) (33%, *E*/*Z* = 50/50),[8] and no desired product that was envisioned in eq 1 was detected. A dramatic change occurred when this reaction was conducted at 15 °C: the (1-siloxyvinyl)silane **5** was produced in 86% yield.[9] This indicates that the lithium enolate **3** (R = H, G = Me$_3$Si) has been formed as the result of the silicon shift (eq 1). Further examples of the reaction of α-silylalkylithium **1**[5c,10] with carbon monoxide at 15 °C are given in Table I. By quenching with H$_2$O or Me$_3$SiCl, acylsilanes or their enol silyl ethers were conveniently obtained, respectively, in good yields. Interestingly, the formation of these enolates took place in highly stereoselective manner to give *E* enolates exclusively or predominantly, as shown by the structures of products in runs 4, 6, 8, and 11.[11] The enolates undergo standard enolate reactions such



(2)

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[1] See, for example: (a) Wittig, G. *Angew. Chem.* **1940**, *53*, 241. (b) Ryang, M.; Tsutsumi, S. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 1121. (c) Jutzi, P.; Schröder, F. -W. *J. Organomet. Chem.* **1970**, *24*, 1. (d) Trzupek, L. S.; Newirth, T. L.; Kelly, E. G; Sbarbati, N. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 8118. An excellent review of previous works is given in ref 3.

[2] Recent efforts for synthesis via aryllithium and CO, see: (a) Nudelman, N. S.; Vitale, A. A. *J. Org. Chem.* **1981**, *46*, 4625; (b) *Org. Prep. Proced. Int.* **1981**, *13*, 144. (c) Nudelman, N. S.; Outumuro, P. *J. Org. Chem.* **1982**, *47*, 4347. (d) Nudelman N. S.; Vitale, A. *J. Organomet. Chem.* **1983**, *241*, 143.

[3] (a) Seyferth, D.; Weinstein, R. M. *J. Am. Chem. Soc.* **1982**, *104*, 5534. (b) Seyferth, D.; Weinstein, R. M.; Wang, W.-L. *J. Org. Chem.* **1983**, *48*, 1144; (c) *Ibid.* **1983**, *48*, 3367. (d) Seyferth, D; Weinstein, R. M.; Wang, W.-L.; Hui, R. C. *Tetrahedron Lett.* **1983**, *24*, 4907.

[4] The Δ*E* value between **2** and **3** where R,G = H (not lithium salt) has been estimated as ca. 28 kcal/mol; see: Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5612.

[5] (a) West, R. *Adv. Organomet. Chem.* **1977**, *16*, 1. (b) Brook, A. G.; Bassindale, A. R. "Rearrangement in Ground and Excited States"; Mayo, P. de, Ed.; Academic Press: New York, 1980; Vol. 2, pp 149–227. (c) Colvin, E. W. "Silicon in Organic Synthesis"; Butterworths: London, **1980**. (d) Eisch, J. J.; Tsai, M.-R. *J. Am. Chem. Soc.* **1973**, *95*, 4065.

[6] A portion of this work has been taken from: Iriguchi, J. B. S. Thesis Osaka Univesity Suita, Osaka, Japan, 1982. Also presented at the 47th Annual Meeting of Chemical Society of Japan, Kyoto, Japan, April 1, 1983; abstract Vol. II, p 820.

[7] Prepared from Me$_3$SiCH$_2$Cl and Li dispersion containing 1% Na (Ventron Co.) in ether (−15 °C, 4 h)[a,b] and titrated by *N*-benzylidenebenzylamine/PhCOOH/THF.[c] (a) Sommer, L. H.; Murch, R. M.; Mitch, F. A. *J. Am. Chem. Soc.* **1954**, *76*, 1619. (b) Connoly, J. W.; Urry, G. *Inorg. Chem.* **1963**, *2*, 645. (c) Duhamel, L.; Plaquevent, J. C. *J. Org. Chem.* **1979**, *44*, 3404.

[8] The authentic sample of **4** was separately prepared from ethyl (trimethylsilyl)acetate (Na/Me$_3$SiCl/Et$_2$O, 35 °C, 17 h, 30% yield, *E*/*Z* = 18/82). See: Cookson, C. M.; Whitham, G. H. *J. Chem. Soc., Perkin Trans. 1* **1975**, 806.

[9] Representative procedure: the ethereal solution of Me$_3$SiCH$_2$Li (5 mmol, 4.5 mL of a 1.1 mol/L solution in ether) was degassed and exposed to carbon monoxide from a CO baloon (1 atm) at 15 °C. Gradual CO absorption was observed and after 1.5 h Me$_3$SiCl (5 mmol) was added. The product **5** was distilled directly from the mixture (75% yield). **5**: bp 73–80 °C (90 mm); ^{1}H NMR (CCl$_4$) δ 0.06 (s, 9 H, CSi(CH$_3$)$_3$), 0.17 (s, 9 H, OSi(CH$_3$)$_3$), 4.43 (d, *J* = 4 Hz, 1 H, HC=), 4.71 (d, *J* = 4 Hz, 1 H, HC=); IR (neat) ν 1590 cm^{-1} (C=C); mass spectrum, *m*/*e* 188 (M$^+$, 20), 173 (M$^+$ − 15, 24), 147 (100), 73 (100). **5** is a known compound, see: Bourgeois, P.; Dunogues, J.; Duffaut, N. *J. Organomet. Chem.* **1974**, *80*, C25. All new compounds have been fully characterized; see the supplementary material.

[10] Weber, W. P. "Silicon Reagents for Organic Synthesis"; Springer Verlag: Berlin, 1983.