34496-58-7; *p*-dinitrobenzene radical anion, 34505-33-4; *o*-dinitrobenzene radical anion, 34505-38-9; *p*-nitrobenzaldehyde radical anion, 34512-33-9; *m*-nitrobenzaldehyde radical anion, 40951-85-7; 1-chloro-4-nitrobenzene radical anion, 34473-09-1; 5-nitro-*m*-xylene radical anion, 39933-64-7; 3-nitro-*o*-xylene radical anion, 83-41-0; 4-cyano-*N*-benzylpyridinium radical, 113249-25-5; 4-cyano-*N*-methylpyridinium radical, 64365-84-0; 4-carbethoxy-*N*-benzylpyridinium radical, 76036-35-6; 4-carbethoxy-*N*-methylpyridinium radical, 75302-27-1; 4-amido-*N*-benzylpyridinium radical, 113249-26-6; 4-amido-*N*-methylpyridinium radical, 113249-24-4.

Insertion of Two CO Moieties into an Alkene Double Bond To Form a RCH=C(O)C(O)=CHR^{2-} Unit via Organosamarium Activation[1]

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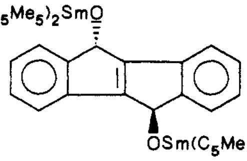
Abstract: RCH═CHR (R = 2-pyridyl) reacts with $(C_5Me_5)_2Sm(THF)_2$ to form a red complex, which reacts with CO at 80 psi in toluene to form $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^4\text{-}RCH{=}C(O)C(O){=}CHR]$ (**1**) in 90% yield. **1** cocrystallizes with 2 molecules of toluene in space group *C2/m* with a = 15.818 (2) Å, b = 14.060 (2) Å, c = 15.353 (2) Å, β = 111.480 (12)°, and Z = 2 for D_{calcd} = 1.32 g cm^{-3}. Least-squares refinement on the basis of 2526 observed reflections led to a final R value of 0.045. The two $(C_5Me_5)_2Sm$ units are bridged by a tetradentate bisenolate ligand, RCH═C(O)C(O)═CHR^{2-}, such that each Sm is coordinated to one oxygen and the nitrogen atom of the pyridyl group closest to that oxygen. The Sm–O, Sm–N, and average Sm–C(ring) distances are 2.191 (6), 2.473 (7), and 2.71 (1) Å, respectively.

The divalent organosamarium complex $(C_5Me_5)_2Sm(THF)_2$[2] has proven to have a remarkable reductive chemistry with unsaturated substrates such as C≡O,[3,4] RC≡CR,[4-7] and RN═NR.[8,9] This powerful Sm(II) reagent can induce facile multiple-bond cleavage and reorganization to provide unusual transformations of multiply bonded species. Three examples are shown in eq 1–3. If C═C double bonds could also be transformed in unusual ways by $(C_5Me_5)_2Sm(THF)_2$, then this organosamarium(II) approach to multiple-bond functionalization would apply to an even wider range of substrates. We report here the samarium-mediated functionalization of a C═C bond in which complete cleavage of the double-bond and double CO insertion is observed.

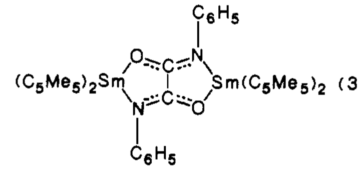
$$4(C_5Me_5)_2Sm(THF)_2 + 6CO \rightarrow [[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^3\text{-}O_2CC{=}C{=}O](THF)]_2 + 6THF \quad (1)^3$$

$$2(C_5Me_5)_2Sm(THF)_2 + C_6H_5C{\equiv}CC_6H_5 + 2CO \longrightarrow$$



(2)[4]

$$2(C_5Me_5)_2Sm(THF)_2 + C_6H_5N{=}NC_6H_5 + 2CO \longrightarrow$$



(3)[9]

Table I. Crystal Data and Summary of Data Collection and Structure Refinement for $(C_5Me_5)_2Sm[\mu\text{-}\eta^4\text{-}(C_5H_4N)CH{=}C(O)C(O){=}CH(C_5H_4N)]Sm(C_5Me_5)_2{\cdot}2C_7H_8$

formula	$Sm_2C_{68}H_{86}N_2O_2$
mol wt	1264.15
space gp	*C2/m*
a, Å	15.818 (2)
b, Å	14.060 (2)
c, Å	15.353 (2)
β, deg	111.480 (12)
V, Å^3	3177
Z	2
D_{calcd}, g/cm^3	1.32
temp, °C	24
λ(Mo Kα), Å	0.71 073; graphite monochromator
μ, cm^{-1}	18.8
min–max transmissn coeff	0.339–0.449
type of scan	θ–2θ
scan width, deg	−1.2 in 2θ from Kα_1 to +1.2 from Kα_2
scan speed, deg/min	3
bkgd counting	evaluated from a 96-step peak profile
data collecn range, deg	3–50
total no. of unique data	2955
no. of unique data with $I \geq 3\sigma(I)$	2526
no. of parameters	187
$R(F)$	0.045
$R_w(F)$	0.059
GOF	1.84
max Δ/σ in final cycle	0.39

Experimental Section

The complexes described below are extremely air- and moisture-sensitive. Therefore, both the syntheses and subsequent manipulations of these compounds were conducted under nitrogen with rigorous exclusion of air and water by Schlenk, vacuum-line, and glovebox techniques. The preparation of $(C_5Me_5)_2Sm(THF)_2$ and the methods for drying solvents

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and taking physical measurements have been described previously.[2] 1,2-Di-2-pyridylethene (Aldrich) was degassed at room temperature. CO (Liquid Carbonic, 99.99%) was used as received.

[$(C_5Me_5)_2Sm]_2[\mu$-η^4-$(NC_5H_4)CH{=}C(O)C(O){=}CH(NC_5H_4)$]. 1,2-Di-2-pyridylethene, $(NC_5H_4)CH{=}CH(NC_5H_4)$ (40 mg, 0.221 mmol), in 4 mL of toluene was slowly added to $(C_5Me_5)_2Sm(THF)_2$ (250 mg, 0.442 mmol) in 10 mL of toluene to form a red solution. The solution was placed in a 3-oz Fisher–Porter aerosol reaction vessel and pressurized with CO to 80 psi. After 24 h, the resulting yellow-orange solution was depressurized, concentrated to about half-volume, and cooled to −34 °C. Yellow-orange crystals of **1** (180 mg, 65%) were obtained. The ^1H NMR spectrum of the bulk reaction mixture indicated that **1** was the major product (90% yield). Analytical, NMR, and IR data were obtained on samples of crystals that were crushed to a powder and dried under vacuum. Anal. Calcd for $[(C_5Me_5)_2Sm]_2(C_{14}H_{10}N_2O_2)$: Sm, 27.8. Found: Sm, 27.0. ^1H NMR (C_4D_8O): δ 5.48 (s, 1 H), 5.09 (t, 1 H), 4.97 (d, 1 H), 1.52 (s, 30 H, C_5Me_5). ^{13}C NMR (C_4D_8O): δ 201.1 (s), 140.0 (s), 121.3 (d, J_{CH} = 164 Hz), 119.4 (s, C_5Me_5), 112.2 (d, J_{CH} = 166 Hz), 103.2 (d, J_{CH} = 153 Hz), 18.7 (q, J_{CH} = 125 Hz, C_5Me_5). IR (KBr): 2960–2850 s, 2730 w, 1600 m, 1570 m, 1475 s, 1455 s, 1430 s, 1380 s, 1205 w, 1155 m, 1115 m, 1020 w, 995 m, 865 m, 800 m, 755 w, 740 m, 730 m cm^{-1}.

X-ray Data Collection, Structure Solution, and Refinement for [$(C_5Me_5)_2Sm]_2[\mu$-η^4-$(NC_5H_4)CH{=}C(O)C(O){=}CH(NC_5H_4)]\cdot 2C_7H_8$. General data collection and reduction procedures have been described previously.[10,11] A single crystal measuring 0.40 mm × 0.50 mm × 0.60 mm was sealed under nitrogen in a glass capillary and mounted on a Nicolet R3m/V diffractometer. Lattice parameters were determined from 25 computer-centered reflections. Data were collected by the θ–2θ scan technique in bisecting geometry. The *p* factor in the expression[12] for the standard deviation of the observed intensities was given a value of 0.05. Crystal and data collection parameters are given in Table I. During the data collection, the intensities of three standard reflections measured every 100 reflections exhibited only random fluctuations within ±3%. An empirical absorption correction was applied. Only one systematic absence (*hkl*, *h* + *k* odd) established the space group as *C*2 or *C*2/*m*. Solution and refinement of the structure showed *C*2/*m* to be the correct choice. Refinement was also tried in space group *C*2 but was not successful.[13]

MITHRIL[14] and difference Fourier techniques were used to locate all non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic temperature factors by full-matrix least-squares methods. Only the hydrogen atoms of the $(NC_5H_4)CHC(O)C(O)CH(NC_5H_4)^{2-}$ unit were included with their idealized positions (C–H = 0.95 Å). Atomic scattering factors were taken from ref 15. A final difference map contained no recognizable features; its largest peak was of height 0.92 e $Å^{-3}$. Fractional coordinates are given in the supplementary material.

Results and Discussion

Given the success observed in $(C_5Me_5)_2Sm(THF)_2$-based transformations of the diphenyl-substituted substrates, $C_6H_5C{\equiv}CC_6H_5$[4] and $C_6H_5N{=}NC_6H_5$[9] (eq 2 and 3), the diphenyl-substituted alkene $C_6H_5CH{=}CHC_6H_5$ seemed to be a logical substrate with which to investigate C=C bond reactivity. Although $(C_5Me_5)_2Sm(THF)_2$ reacts with *trans*-$C_6H_5CH{=}CHC_6H_5$[16] in the presence of CO, definitive characterization of the organometallic products by X-ray crystallography has not yet been obtained. A nitrogen-substituted analogue of stilbene, namely 1,2-di-2-pyridylethene, $(NC_5H_4)CH{=}CH(NC_5H_4)$, was chosen as an alternative substrate since the extra coordination possible via the nitrogen atoms could lead to a more readily definable, crystalline product.

Synthesis. Addition of a toluene solution of 1,2-di-2-pyridylethene to $(C_5Me_5)_2Sm(THF)_2$ in toluene forms a red solution, which reacts with CO at 80 psi. After 24 h, the solution had the yellow-orange color characteristic of a Sm^{3+} organometallic complex,[6] and ^1H NMR spectroscopy showed a single primary product had been formed. Crystals suitable for X-ray crystallography were obtained, and the product of the reaction was identified as $[(C_5Me_5)_2Sm]_2[\mu$-η^4-$(NC_5H_4)CH{=}C(O)C(O){=}CH(NC_5H_4)]$ (**1**).

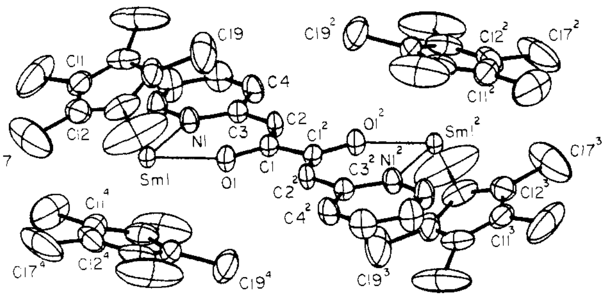

Figure 1. ORTEP plot of $(C_5Me_5)_2Sm[\mu$-η^4-$(C_5H_4N)CH{=}C(O)C(O){=}CH(C_5H_4N)]Sm(C_5Me_5)_2$. Thermal ellipsoids are shown at 30% probability for clarity. Atoms without superscript labels are related to atoms with superscript 2 by a C_2 axis and to atoms with superscript 4 by a mirror plane. Superscript 3 atoms are related to superscript 2 atoms by a mirror plane.

Table II. Interatomic Distances (Å) and Angles (deg) for **1**

Sm(1)–O(1)	2.191 (6)	O(1)–Sm(1)–N(1)	76.5 (2)
Sm(1)–N(1)	2.473 (7)	C(1)–O(1)–Sm(1)	138.3 (6)
Sm(1)–C(10)	2.678 (8)	C(3)–N(1)–C(7)	118.0 (8)
Sm(1)–C(11)	2.699 (8)	C(3)–N(1)–Sm(1)	128.8 (6)
Sm(1)–C(14)	2.726 (8)	C(7)–N(1)–Sm(1)	113.2 (6)
S(1)–C(12)	2.728 (8)	O(1)–C(1)–C(2)	125.0 (8)
Sm(1)–C(13)	2.735 (8)	O(1)–C(1)–C(1)	115.7 (10)
O(1)–C(1)	1.299 (10)	C(2)–C(1)–C(1)	119.3 (10)
N(1)–C(3)	1.343 (11)	C(1)–C(2)–C(3)	129.1 (7)
N(1)–C(7)	1.351 (12)	N(1)–C(3)–C(4)	118.2 (8)
C(1)–C(2)	1.355 (12)	N(1)–C(3)–C(2)	122.3 (8)
C(1)–C(1)	1.488 (17)	C(4)–C(3)–C(2)	119.5 (8)
C(2)–C(3)	1.436 (12)	C(5)–C(4)–C(3)	120.7 (10)
C(3)–C(4)	1.429 (13)	C(6)–C(5)–C(4)	119.8 (9)
C(4)–C(5)	1.361 (16)	C(5)–C(6)–C(7)	118.3 (10)
C(5)–C(6)	1.337 (17)	N(1)–C(7)–C(6)	124.9 (10)
C(6)–C(7)	1.352 (14)	C(11)–C(10)–C(14)	107.4 (8)
C(10)–C(11)	1.367 (15)	C(11)–C(10)–C(16)	126.0 (16)
C(10)–C(14)	1.418 (14)	C(14)–C(10)–C(16)	126.6 (16)
C(10)–C(16)	1.555 (14)	C(12)–C(11)–C(10)	109.4 (9)
C(11)–C(12)	1.295 (14)	C(12)–C(11)–C(15)	124.3 (17)
C(11)–C(15)	1.541 (15)	C(10)–C(11)–C(15)	125.6 (17)
C(12)–C(13)	1.349 (13)	C(11)–C(12)–C(13)	110.1 (8)
C(12)–C(17)	1.545 (15)	C(11)–C(12)–C(17)	123.8 (14)
C(13)–C(14)	1.385 (16)	C(13)–C(12)–C(17)	126.0 (14)
C(13)–C(18)	1.535 (14)	C(12)–C(13)–C(14)	109.0 (8)
C(14)–C(19)	1.530 (14)	C(12)–C(13)–C(18)	128.1 (14)
C(20)–C(21)	1.34 (2)	C(14)–C(13)–C(18)	122.7 (14)
C(20)–C(24)	1.37 (3)	C(13)–C(14)–C(10)	104.2 (8)
C(21)–C(22)	1.36 (3)	C(13)–C(14)–C(19)	127.3 (15)
C(22)–C(23)	1.33 (2)	C(10)–C(14)–C(19)	128.4 (15)
		C(21)–C(20)–C(21)	123 (2)
		C(21)–C(20)–C(24)	119 (1)
		C(20)–C(21)–C(32)	115 (2)
		C(23)–C(22)–C(21)	128 (2)
		C(22)–C(23)–C(22)	111 (3)

Structure. The structure of **1** is shown in Figure 1, and bond distances and angles are given in Table II. The molecule has crystallographic C_{2h} symmetry, with the mirror plane containing O(1), C(1), C(2), Sm(1), and the pyridyl rings. The C_2 axis bisects the C(1)–C(1^2) bond.

The C(1)–C(1^2) distance of 1.488 (17) Å is in the range commonly observed for sp^2–sp^2 single bonds. The C(1)–C(2) and C(2)–C(3) distances of 1.355 (12) and 1.436 (12) Å, respectively, fall between the normal ranges for C–C single and double bonds[17] and suggest that some delocalization of the multiple bond is

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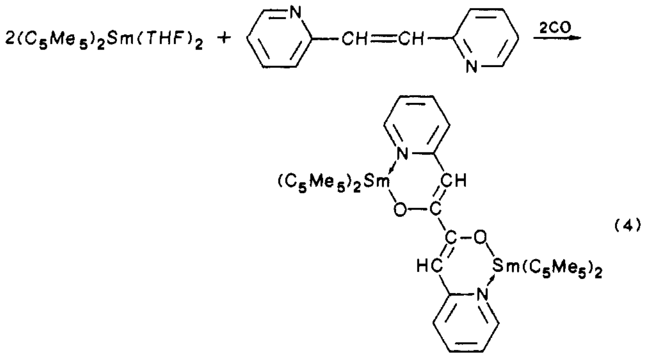
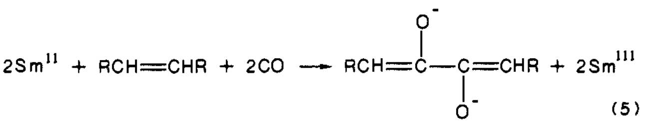
occurring. The C–O, C–N, Sm–O, and Sm–N distances are also consistent with a delocalized picture. The C(1)–O(1) and C(3)–N(1) distances of 1.299 (10) and 1.343 (11) Å, respectively, are intermediate between single and double bonds.[18] The Sm–O(1) distance of 2.191 (6) Å and the Sm–N(1) distance of 2.473 (7) Å are between the values typical for trivalent Ln–OR and $Ln-NR_2$ bonds and $R_2O \rightarrow Ln$ and $R_3N \rightarrow Ln$ donor bonds.[3,8,19] Hence, the new planar ligand may be formally viewed as a $(C_5H_4N)CH{=}C(O)C(O){=}CH(C_5H_4N)^{2-}$ dianion with considerable delocalization.

The average Sm–C(ring) distance, 2.71 (1) Å, is on the low end of the range typical for trivalent $(C_5Me_5)_2Sm(X)(Y)$ complexes,[20] and the (ring centroid)–Sm–(ring centroid) angle, 140.8°, is at the high end of the normal range.[2] The pentamethylcyclopentadienyl rings are in the unusual eclipsed conformation. In the past, the presence of eclipsed C_5Me_5 rings in organolanthanide complexes has been attributed to steric crowding in other parts of the molecule.[21] However, several examples of structures with eclipsed rings have been reported recently in which the steric crowding is not so obvious.[9,22,23] Complex **1** is another example of this latter trend.

Reaction. The structure of **1** shows that two molecules of carbon monoxide have been inserted into the carbon–carbon double bond of 1,2-di-2-pyridylethene as shown in eq 4. To our knowledge, the formal insertion of two molecules of CO into a carbon–carbon double bond is unprecedented in organic and organometallic chemistry. The net transformation (eq 5) of a C=C double bond into a bisenolate may indicate a new avenue of alkene derivatization in organic synthesis.





$$2Sm^{II} + RCH{=}CHR + 2CO \longrightarrow RCH{=}C(O^-)-C(O^-){=}CHR + 2Sm^{III} \qquad (5)$$

The reaction is formally similar to the double insertion of two CO molecules into the N=N bond of azobenzene (eq 3).[9] It is interesting to note that **1** and the product of reaction 3 have the same formula; i.e., they differ only in the position of the nitrogen atoms. They also crystallize in equivalent space groups. Detailed mechanistic studies will be necessary to determine whether the transformations in reactions 3 and 4 actually proceed by a similar pathway. It is likely, however, that in both cases the strong reduction potential of $(C_5Me_5)_2Sm(THF)_2$ is important in activating the unsaturated substrate and the oxophilicity of samarium[24] is important in the CO activation. Superficially, it appears that the pyridyl substituents have been useful in leading to a fully definable product. The importance of the nitrogen atoms in guiding the reaction remains to be determined.

Conclusion

The use of Sm(II) in organic chemistry is rapidly growing.[25-31] This study demonstrates that the facile conversion of an alkene to a bisenolate is another transformation that is possible via Sm(II). These results also show that the appropriate substitution of nitrogen for carbon can facilitate characterization of these organosamarium reactions.

Acknowledgment. We thank the National Science Foundation for support of this research and Professor Robert J. Doedens and Dr. Joseph W. Ziller for helpful discussions.

Registry No. 1, 113303-24-5; $(C_5Me_5)_2Sm(THF)_2$, 79372-14-8; $(N-C_5H_4)CH{=}CH(NC_5H_4)$, 1437-15-6.

Supplementary Material Available: Table of positional parameters and thermal parameters (1 page); table of observed and calculated structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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