yield) of $PhMe_2SiCl$:[8] bp 76–77 °C/12 mmHg.

Preparation of Chloromethyldiphenylsilane (2b). A mixture of 10.7 g (53.8 mmol) of Ph_2MeSiH,[9] 13.8 g (102.9 mmol) of anhydrous $CuCl_2$, and 0.297 g (1.56 mmol) of anhydrous CuI in 250 mL of ether was stirred at room temperature for 21 h. The mixture was filtered, and the filtrate was concentrated. The residue was fractionally distilled under reduced pressure to give 9.7 g (77% yield) of $Ph_2MeSiCl$:[10] bp 85–86 °C/0.5 mmHg.

Preparation of Dibutylchloromethylsilane (3b). A mixture of 14.8 g (93.7 mmol) of Bu_2MeSiH,[11] 26.0 g (193.2 mmol) of anhydrous $CuCl_2$, and 0.910 g (4.76 mmol) of anhydrous CuI in 200 mL of ether was stirred at room temperature for 70 h. The mixture was fractionally distilled under reduced pressure to give 15.8 g (87% yield) of $Bu_2MeSiCl$:[11] bp 92–94 °C/16 mmHg.

Reaction of Iodotrimethylsilane with $CuCl_2$. Iodotrimethylsilane (bp 106.5 °C) was prepared by the reaction of hexamethyldisilane and iodine.[23] Into a suspension of $CuCl_2$ (23.2 g, 172.6 mmol) in di-*n*-butyl ether (200 mL), was added Me_3SiI (17.0 g, 84.8 mmol) over 10 min. The mixture was stirred at room temperature, and the progress of the reaction was monitored by GLC. After 10 min, the peak due to the iodosilane diminished to half and a new peak due to chlorotrimethylsilane appeared. All of the iodosilane completely disappeared within 30 min. The reaction mixture was filtered to remove copper salts. The filtrate was distilled through a short distillation column under atmospheric pressure to give 6.41 g (59.0 mmol, 70% yield) of Me_3SiCl:[24] bp 57 °C; ^1H NMR (δ in C_6D_6) 0.23 (SiMe); ^{13}C NMR (δ in C_6D_6) 3.00 (SiMe).

Registry No. **1a**, 766-77-8; **1b**, 768-33-2; **2a**, 776-76-1; **2b**, 144-79-6; **3a**, 999-35-9; **3b**, 996-07-6; **4a**, 542-91-6; **4b**, 1609-19-4; **5a**, 766-08-5; **5b**, 1631-82-9; **6a**, 694-53-1; **6b**, 4206-75-1; **7b**, 1631-84-1; **8a**, 7535-09-3; **8b**, 141557-03-1; **9b**, 85590-06-3; **10a**, 18410-59-8; **10b**, 141557-04-2; **11b**, 29442-41-9; **12a**, 29681-57-0; **12b**, 18162-48-6; iodotrimethylsilane, 16029-98-4; chlorotrimethylsilane, 75-77-4.

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Stepwise and Reversible Cleavage of the C–O Double Bond of Diaryl Ketones by Lanthanide Metals

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Summary: Reaction of diaryl ketones with excess lanthanide (Ln = Sm, Yb) metals caused the complete cleavage of their C–O double bonds. This C–O bond-cleavage process was stepwise and reversible and was possibly mediated by a *μ*-oxo, *μ*-alkylidene complex.

It has been reported that reaction of diaryl ketones with lanthanide metals gives corresponding dianions that possess high nucleophilic reactivity.[1] We have recently isolated and structurally characterized one of these dianionic compounds,[2] and during this study we have found that further reaction of these dianionic compounds or their parent diaryl ketones with excess lanthanide metals led to complete cleavage of their C–O bonds and gave the corresponding deoxygenation products after hydrolysis.

There have been many reports on the C–O bond cleavage of ketones and aldehydes which is promoted by metals or metal complexes.[3-6] A few mechanisms have been proposed for the C–O bond-cleavage process. In the reaction of active titanium metal or some metal alkylidene

Table I. Reaction of Diaryl Ketones with Lanthanide Metals[a]

Ln[b]	ketone	Ln:ketone	reacn time	product distribn[c] (amt, %)
Yb	benzophenone	3:1	4 h	benzhydrol (100), diphenylmethane (0)
			1 day	benzhydrol (90), diphenylmethane (10)
Sm	benzophenone	3:1	4 h	benzhydrol (92), diphenylmethane (8)
			1 day	benzhydrol (85), diphenylmethane (15)
Sm	9-fluorenone	2:1	1 day	9-fluorenol (71), fluorene (29)
		5:1	1 day	9-fluorenol (66), fluorene (34)
			3 days	9-fluorenol (35), fluorene (65)

[a] Room temperature in THF/HMPA. [b] The metals were activated with 2% of ICH_2CH_2I. [c] Molar ratio determined by ^1H NMR spectroscopy. The conversion of the reactions was 100%.

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[‡] Hiroshima University.

[§] Kyushu University.

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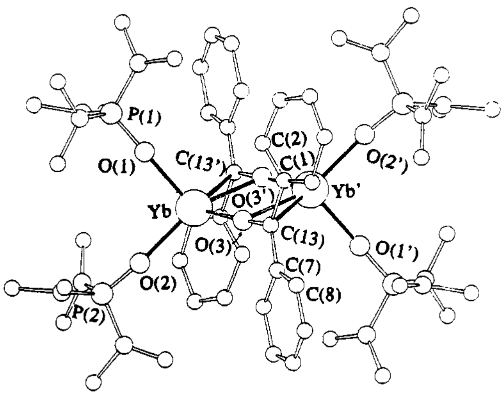


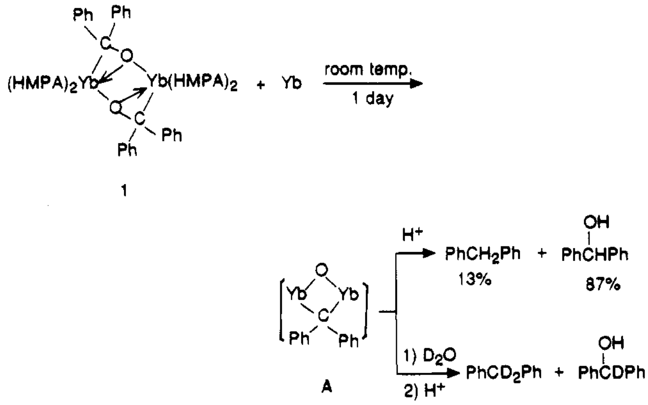
Figure 1. ORTEP drawing of 1. Selected bond lengths (Å) and angles (deg): Yb···Yb', 3.508 (4); Yb–O(1), 2.27 (3); Yb–O(2), 2.28 (2); Yb–O(3), 2.11 (3); Yb–O(3'), 2.39 (2); Yb–C(13'), 2.59 (5); C(13)–O(3), 1.39 (6); O(1)–Yb–O(2), 93 (1); O(2)–Yb–O(3), 105 (1); O(1)–Yb–O(3), 110 (1); O(1)–Yb–C(13'), 99(1); O(2)–Yb–C(13'), 134 (1); O(3)–Yb–C(13'), 110 (1); C(13)–O(3)–Yb, 172 (3); Yb–O(3)–Yb', 102 (1); C(13)–O(3)–Yb', 82 (2); O(3)–C(13)–C(1), 117 (3); O(3)–C(13)–C(7), 118 (4); C(1)–C(13)–C(7), 123 (4).

complexes with ketones and aldehydes, for example, the C–O bond cleavage is thought to be achieved via the deoxygenation of pinacolate or oxametallacycle intermediates,[3,4] whereas in the case of some electron-rich tungsten complexes, four-electron oxidative addition to the metal center occurs to give metal oxo–alkylidene complexes.[5] In the reaction of divalent lanthanide complexes RLnI with α,β-unsaturated ketones and aldehydes, a π-allyl type intermediate was proposed.[6] The C–O bond cleavage of monoxide by a divalent samarium complex was also reported.[7] None of these C–O bond-cleavage processes have been reported to be reversible. We have now found that, in the reaction of diaryl ketones with lanthanide metals, the C–O bond-cleavage process is different from those mentioned above. It is a stepwise and reversible process and is possibly mediated by a μ-oxo, μ-alkylidene intermediate that has not been mentioned to date.

Results and Discussion

As previously reported, the reaction of diaryl ketones with lanthanide metals greatly depends on their ratios.[1a,c,d] For example, in the reaction of benzophenone with Yb metal 0.5 equiv of Yb gives selectively the reductive coupling product benzopinacol, while 1 equiv of Yb results in the sole formation of the reduction product benzhydrol.[1a,c] One might expect that using a large excess of the metal could achieve further reduction. Table I summarizes the results of the reaction of diaryl ketones with lanthanide metals under various conditions. The further reduced product diphenylmethane was indeed obtained when 3 equiv of Yb metal was used in the reaction with benzophenone. Sm metal showed stronger reducing power under similar conditions,[8] and in the reaction with fluorenone, 5 equiv of Sm resulted in the formation of 65% of fluorene together with 35% of fluorenol after 3 days.[9] Diphenylmethane-d_2 or fluorene-d_2 was obtained when these reactions were quenched with D_2O. This suggests the existence of the intermediates which have a α-dianion structure (vide infra). The reaction of alkyl or monoaryl ketones under similar conditions gave only the corresponding self-coupling products,[1a] and no deoxygenation products were obtained.

Scheme I



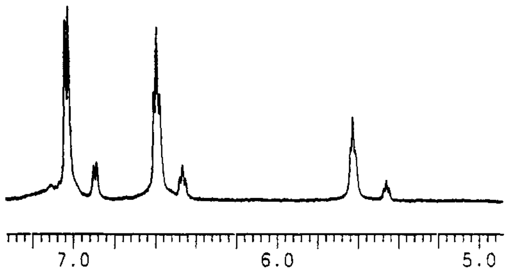


Figure 2. Phenyl part of the ^{1}H NMR spectrum of the mixture of 1 and the alkylidene A.

In the reaction of benzophenone with 1 equiv of Yb metal an Yb(II)–benzophenone dianionic complex, [Yb(OCPh$_2$)(HMPA)$_2$]$_2$ (1), was isolated. Its X-ray crystal structure and selected bond lengths and angles are shown in Figure 1.[2,10] Two Yb atoms are bridged by two benzophenone dianions. The bridge is built in such a manner that a benzophenone dianion uses its O$^-$ atom to make a Yb–O bond with one Yb(II) ion and its C$^-$ atom to form a Yb–C bond with the other Yb(II) ion to which the lone electron pair of the oxygen atom is also donated. The C–O bond distance of the benzophenone ligand in 1 (1.39 (6) Å) is longer than that of free benzophenone (1.23 Å)[11] and can be considered as a C–O single bond.[5c,12] The sum of the angles formed by O(3), C(1), and C(7) around C(13) is 358°, suggesting that C(13) is still sp^2-hybridized and 1 should be a true ketone dianion metal complex. This is consistent with the fact that complex 1 is formed via two-electron transfer from Yb metal to benzophenone. The ^{1}H NMR spectrum of complex 1 showed a great upfield shift for the signals of the phenyl groups in benzophenone, which appeared as a doublet and two triplets at δ 7.04, 6.59, and 5.63, respectively. This also suggests a large electron density increase in the benzophenone ligand of complex 1.

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(8) The activity of lanthanide metals seems to depend on the activation methods. See also ref 1a–d.

(9) Fluorene formation was recently mentioned in the reaction of an excess of samarium metal with fluorenone in dimethoxymethane.[1d]

(10) Crystal data for 1: $C_{25}H_{46}N_6O_3P_2Yb$, M_r = 713.62, triclinic, space group $P\bar{1}$ (No. 2), a = 12.897 (3) Å, b = 12.990 (3) Å, c = 10.480 (2) Å, α = 109.80 (2)°, β = 92.79 (2)°, γ = 74.43 (2)°, V = 1589.6 Å^3, Z = 2, D_c = 1.491 g cm^{-3}, μ(Cu Kα) = 1.644 cm^{-1}, R = 0.108 (R_w = 0.129) for 1805 unique data with $F_o \geq 6\sigma(F_o)$. All attempts to obtain a better crystal were unsuccessful because of the extreme air and moisture sensitivity of the compound.

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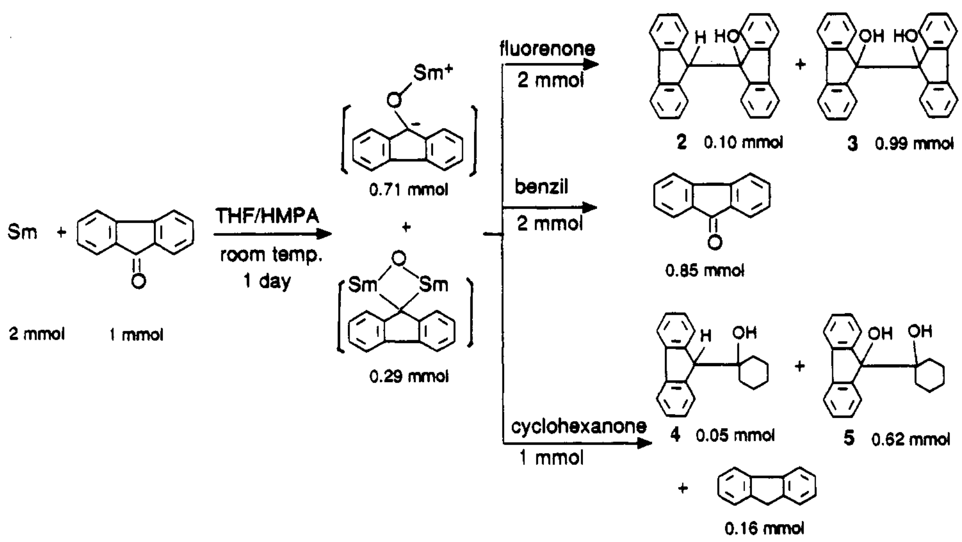
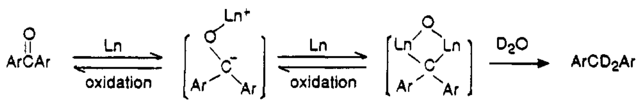
Scheme II



The reaction of complex 1 with excess Yb metal gave 13% of the deoxygenation product Ph_2CH_2, after hydrolysis, and again the corresponding deuterated product, Ph_2CD_2, was formed on quenching the reaction with D_2O (Scheme I). The precursor of Ph_2CH_2 could be obtained together with complex 1 as red-black fine crystals. Its ^1H NMR signals for the phenyl groups appeared as one doublet and two triplets at δ 6.90, 6.47, and 5.46, respectively, which were clearly further shifted upfield compared with those of complex 1 (Figure 2). This upfield shift indicates that there is a further electron density increase in the phenyl groups of the C–O bond-cleavage product and is consistent with the consideration of an α-dianion intermediate. Interestingly, on treatment of the reaction mixture with excess benzil, the broken C–O bond was formed again and benzophenone was given in 90% isolated yield.[13] This suggests that the oxygen atom and the carbon atom in the intermediate are located so near to each other that they can make a C–O bond on losing electrons and excludes the possibility of the presence of an oxo (M=O) intermediate as in the case of tungsten complexes.[5] Another characteristic of this reaction which differs from the reactions of tungsten complexes is that the dianionic complex 1 itself does not give any C–O bond-cleavage products. In the THF-d_8 solution of complex 1, no changes were observed at room temperature even after a few days as monitored by ^1H NMR spectroscopy, while in the case of $W(\eta^2\text{-}O{=}C(CH_2)_3CH_2)_2Cl_2(PMePh_2)_2$, for example, the complex spontaneously decomposes at room temperature into the corresponding tungsten(VI) oxo–alkylidene complex.[5a] These differences are understandable, when it is taken into account that tungsten can usually achieve valences of 0–VI, while for ytterbium and samarium only the states of 0–III are available. The best way to explain the present C–O bond-cleavage process would be by using a μ-oxo, μ-alkylidene (α-dianion) intermediate such as A.

At the present stage, attempts to obtain the μ-alkylidene intermediate in a pure state were unsuccessful, because of its extreme air and moisture sensitivity. However, this does not prevent us from checking its reactivity by using the mixture containing its parent dianion, since the reactivities of the dianionic compounds have been well-known.[1,2] Reaction of the mixture of the alkylidene (0.29 mmol) and the dianion (0.71 mmol),[14] which was obtained from the reaction of fluorenone (1 mmol) with Sm metal (2 mmol), with 2 mmol of fluorenone gave the corresponding coupling products 2 (0.10 mmol) and 3 (0.99 mmol),[1c,d] with 0.55 mmol of fluorenone being recovered (Scheme II). It is worthy of note that the yield of 2 is much less than 0.29 mmol and the yield of 3 is much more than 0.71 mmol. This indicates that the C–O bond re-formation within the alkylidene intermediate also occurred here, which caused its reaction with fluorenone to give 3 rather than 2 and resulted in less formation of 2 and more formation of 3.[15] As in the case of complex 1, reaction of the mixture with 2 mmol of benzil yielded 0.85 mmol of the starting fluorenone. In the reaction with cyclohexanone (1 mmol) under similar conditions, besides the cross-coupling products 4 (0.05 mmol) and 5 (0.62 mmol),[1c] 0.16 mmol of fluorene was obtained (Scheme II). No deuterium was incorporated into the fluorene when the reaction was quenched with D_2O, suggesting the fluorene should be formed via the abstraction of the α-hydrogens of cyclohexanone.[16] In the above reactions no alkene formation was observed, which is in contrast to both the reactions of the early-transition-metal alkylidene complexes[4] and the reactions of the tungsten oxo–alkylidene compounds.[5b–d]

Scheme III



Therefore, the reaction of diaryl ketones with lanthanide metals could be described as shown in Scheme III. The C–O double bond is first reduced to a single one and then is cleaved by a second metal to give a μ-oxo, μ-alkylidene intermediate. Upon oxidation, the cleaved C–O bond is formed again, which thus makes the process reversible. The alkylidene intermediate seems to be more basic than

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(13) Benzil acted here as an electron acceptor and became benzoin after hydrolysis. The oxidation of the dianionic compound to yield benzophenone has been previously mentioned.[1c]

(14) The amounts of the alkylidene and the dianion were estimated on the basis of the assumption that all the alkylidene becomes fluorene and all of the dianion yields fluorenol after hydrolysis (see also Table I).

(15) Product 3 may be formed via the following three reactions: (a) direct addition of the dianion to fluorenone, (b) the reaction of the alkylidene with fluorenone accompanied by the C–O bond re-formation, and (c) the self-coupling of fluorenone promoted by Sm^{2+} or other reducing species.

(16) For a recent example of α-hydrogen abstraction of alkyl ketones by lanthanide carbyl complexes, see: Heeres, H. J.; Maters, M.; Teuben, J. H. *Organometallics* **1992**, *11*, 350.

its parent dianion and can abstract α-hydrogens of an alkyl ketone. The lack of success in the deoxygenation of alkyl or monoaryl ketones would be due to the difficulty in generating the corresponding more unstable μ-alkylidene (α-dianion) intermediates.

Experimental Section

General Methods. All reactions were carried out under a dry and O_2-free Ar atmosphere by using Schlenk techniques. The D_2O quenching experiments were done by treating the reaction mixture first with 1 mL of D_2O and then with 2 N HCl. ^1H NMR spectra of organometallic species were taken in an NMR tube sealed under vacuum. All organic products were identified by melting points and ^1H NMR, IR, and mass spectra, and new compounds were further confirmed by micro elemental analyses. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under Ar prior to use. THF-d_8 was commercial grade and was degassed by the freeze–thaw method (three times) and dried over K. Toluene was distilled from sodium benzophenone ketyl under Ar and dried over K. Hexamethylphosphoramide (HMPA) was distilled under reduced pressure, degassed by the freeze–thaw method (three times), and dried over molecular sieves (4A). Diaryl ketones were obtained from Tokyo Kasei Co. and were recrystallized from methanol. Lanthanide metals (40 mesh) were obtained from Rare Metallic Co. ^1H NMR spectra were recorded on a JNM-GX 400 (FT, 400 MHz) or a FX-90Q (FT, 90 MHz) spectrometer and are reported in ppm downfield from tetramethylsilane. Infrared spectra were recorded on a JASCO A-202 IR spectrometer. Mass spectra were obtained on a JMS-GH-100 apparatus. Melting points were measured on a Yanaco micro melting point apparatus and are uncorrected. Elemental analyses were performed by the chemical analysis laboratory of RIKEN.

Reaction of Diaryl Ketones with Lanthanide Metals. To a proper amount of the metals, which had been treated with 2% of ICH_2CH_2I in THF (4 mL) and HMPA (1 mL), was added a THF (4 mL) solution of diaryl ketones with a syringe. The mixture was then stirred at room temperature for a proper period of time (see Table I). When the deoxygenation reaction occurred, a red-brown (Sm) or wine red (Yb) solution was finally obtained, which was then hydrolyzed with 2 N HCl and extracted with ether (3 × 30 mL). Evaporation of the solvent gave the reduction products, which were isolated with preparative liquid chromatography (silica gel) and identified as mentioned above. Their ratios were obtained by a ^1H NMR determination of the product mixtures (Table I).

Isolation of the Ytterbium(II)–Benzophenone Dianion Complex $[Yb(OCPh_2)(HMPA)_2]_2$ (1). The mixture of Yb metal (173 mg, 1 mmol) and benzophenone (182 mg, 1 mmol) in THF/HMPA (6:1) was stirred at room temperature for 1 h and then filtered into another Schlenk flask. Fine crystals were formed after reducing the volume under vacuum and standing at room temperature overnight. The supernatant was carefully removed by a syringe, and the crystals were washed with toluene and dried under vacuum. Finally, red-black fine crystals of 1 (303 mg, 42%) were obtained: mp 159–160 °C; ^1H NMR (THF-d_8) δ 7.04 (d, J = 7.6 Hz, 8 H, Ph), 6.59 (t, J = 7.6 Hz, 8 H, Ph), 5.63 (t, J = 7.6 Hz, 4 H, Ph), 2.54 (br s, 72 H, NMe); IR (THF) δ_{CO} 1566 cm^{-1}. Anal. Calcd for $C_{50}H_{92}N_{12}O_6P_4Yb_2$: C, 42.08; H, 6.50; N, 11.78. Found: C, 41.80; H, 6.55; N, 11.56.

Reaction of Complex 1 with Yb Metal. To 249 mg (1.44 mmol) of the Yb metal activated with ICH_2CH_2I in THF (4 mL) was added a purple THF (2 mL) solution of 1 (343 mg, 0.24 mmol). The mixture was stirred at room temperature overnight, and finally a wine red solution was obtained. Working up the mixture as mentioned above gave diphenylmethane and benzhydrol in 13% and 87% ^1H NMR yields, respectively. Filtration of the above reaction mixture and evaporation of the solvent gave red-black crystalline products whose ^1H NMR spectrum in THF-d_8 is shown in Figure 2.[17]

The oxidation reaction with benzil was performed as follows. To the reaction mixture, which was obtained from the reaction of 1 (371 mg, 0.26 mmol) with Yb (270 mg, 1.56 mmol) in THF (4 mL) (see above),[18] was added benzil (210 mg, 1 mmol) in THF (4 mL). The resultant green mixture was stirred at room temperature for 1 h and then worked up and separated as above. Benzophenone (85 mg, 0.47 mmol) and benzoin (117 mg, 0.55 mmol) were obtained together with benzil (78 mg, 0.37 mmol).

Reaction of the Alkylidene Mixture with Ketones. The reaction mixture of Sm metal (2 mmol) and fluorenone (1 mmol) (see above and Scheme II) was first filtered into another flask, and a proper amount of ketones was then added. The mixture was stirred at room temperature for 1 h, and the products were worked up and isolated as above.

Physical properties of new compounds are recorded below.

9-(9′-Fluorenyl)-9-fluorenol (2): mp 200–201 °C; ^1H NMR ($CDCl_3$) δ 7.05–7.68 (m, 16 H), 4.03 (s, 1 H), 3.12 (s, 1 H); IR (Nujol) 3565 cm^{-1} (OH); MS m/e 346 (M$^+$). Anal. Calcd for $C_{26}H_{18}O$: C, 90.14; H, 5.24. Found: C, 90.10; H: 5.31.

1-(9-Fluorenyl)cyclohexanol (4): mp 133–135 °C; ^1H NMR ($CDCl_3$) δ 7.03–7.66 (m, 8 H), 4.01 (s, 1 H), 2.30 (br s, 1 H), 0.50–1.65 (m, 10 H); IR (Nujol) 3300 cm^{-1} (OH); MS m/e 264 (M$^+$). Anal. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.41; H, 7.50.

Crystal Structure Determination of Complex 1. Complex 1 could be recrystallized from THF/toluene to give red-black needlelike crystals, from which a crystal of X-ray quality was obtained. The crystal was sealed in a glass capillary under Ar. Data were collected on an Enraf-Nonius CAD4 diffractometer with a rotating anode (20 °C, Cu Kα radiation, λ = 1.541 84 Å, ω scan, 2° ≤ θ ≤ 68°). Lattice constants were obtained by least-squares refinement of the setting angles of 25 reflections with 30° ≤ θ ≤ 35°. Three reflections were monitored periodically as a check for crystal decomposition or movement and a decrease of 5% in intensity was observed. The data were corrected for X-ray absorption effects and for decay. The structure was solved by MULTAN[19] to locate the metal atom, and the remaining non-hydrogen atoms were found from subsequent difference Fourier syntheses. No attempts were made to locate the hydrogen atoms. Refinements were performed by the block-diagonal least-squares method[20] and converged with R = 0.108 and R_w = 0.129. The structure analyses were in both $P1$ and $P\bar{1}$ groups. The results indicate that a center of symmetry exists at the center of the Yb bridge, and so, the space group was assigned as $P\bar{1}$.

Acknowledgment. This work was supported by The Institute of Physical and Chemical Research (RIKEN) and The Science and Technology Agency of Japan under the Special Researchers' Basic Science Program. We thank Prof. D. W. Stephan for reading the manuscript and helpful comments.

Supplementary Material Available: Listings of atomic coordinates, thermal parameters, and bond distances and angles for 1 (3 pages). Ordering information is given on any current masthead page.

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[17] The HMPA part showed a broad singlet at δ 2.48.

[18] The unreacted metal was filtered off.

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