Transfer of Ketyls from Alkali Metals to Transition Metals. Formation and Diverse Reactivities of d-Block Transition-Metal Ketyls

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This paper reports our studies on the preparation of d-block transition-metal ketyls via metathesis reactions of alkali-metal ketyls with transition-metal chlorides as well as via deprotonation of pinacols with a transition-metal base. The metathesis reaction of sodium fluorenone ketyl with $(C_5Me_5)_2ZrCl_2$ in THF gave the corresponding zirconium fluorenone ketyl complex $(C_5Me_5)_2Zr(OC_{13}H_8)Cl$ (**1**), which represents the first example of a structurally characterized d-block transition-metal ketyl complex. In the case of sodium benzophenone ketyl, further reaction between the ketyl radical and a C_5Me_5 ligand took place to give finally the zirconium bis(alkoxide) complex $(\eta^5\text{-}C_5Me_5)(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2C(Ph)_2O)Zr(OCHPh_2)$ (**2**). In contrast, the similar reaction of $[(C_5Me_5)Ir(\mu\text{-}Cl)Cl]_2$ with sodium fluorenone ketyl yielded the iridium carbonyl complex $(C_5Me_5)Ir(CO)(C_{12}H_8)$ (**5**), as a result of decarbonylation of fluorenone. When $[(C_5Me_5)Ir(\mu\text{-}H)Cl]_2$ was used to react with sodium fluorenone or benzophenone ketyl, the dechlorination (reduction) product $[(C_5Me_5)Ir(\mu\text{-}H)]_2$ (**8**), together with fluorenone or benzophenone, formed selectively. The ketone-free **8** could be obtained in high yields by reaction of $[(C_5Me_5)Ir(\mu\text{-}H)Cl]_2$ with 2 equiv of K or Na in THF. The reaction of 1,2-bis(biphenyl-2,2′-diyl)ethane-1,2-diol (**9**) with the iridium imido complex $(C_5Me_5)IrN^tBu$ in THF gave a mixture of **5** (30%) and **8**·2(fluorenone) (30%). However, when the reaction was carried out in benzene, the pinacolate complex $(C_5Me_5)Ir(O_2C_{26}H_{16})$ (**10**) was formed as a major product (73%) together with a small amount of **5** (9%) and **8** (13%).

Introduction

Metal ketyls, which are usually formed via one-electron reduction of ketones or aldehydes by reducing metals, represent one of the most important intermediates in organic chemistry.[1] These highly reactive and synthetically useful species have received continuous attention from a broad range of chemists since their discovery more than 100 years ago.[1,2] The recent successful isolation and structural characterization of a series of alkali-metal, alkaline-earth-metal, and lanthanide-metal ketyl complexes represent one of the highlights in this area.[3−11] However, the previously reported metal ketyls have almost all been limited to those of the metal ions which are good electron transfer agents when in low oxidation states. Ketyl complexes of nonreducing metals, particularly those of the d-block transition metals, have remained unexplored.[12,13]

During our recent studies on structurally well-defined reducing-metal ketyl complexes,[3,4,6,8−10] we became interested in the ketyl complexes of d-block transition metals. In this paper, we report the first structurally

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† The Institute of Physical and Chemical Research (RIKEN).

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[11] Bock, H.; Herrmann, H.-F.; Fenske, D.; Goesmann, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1067.

[12] The formation of silicon ketyl species via C−C bond cleavage of the corresponding pinacolates at high temperature has been previously described. See: (a) Newmann, W. P.; Schroeder, B.; Ziebarth, M. *Liebigs Ann. Chem.* **1975**, 2279. (b) Ziebarth, M.; Newmann, W. P. *Liebigs Ann. Chem.* **1978**, 1765.

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10.1021/om981013c CCC: $18.00
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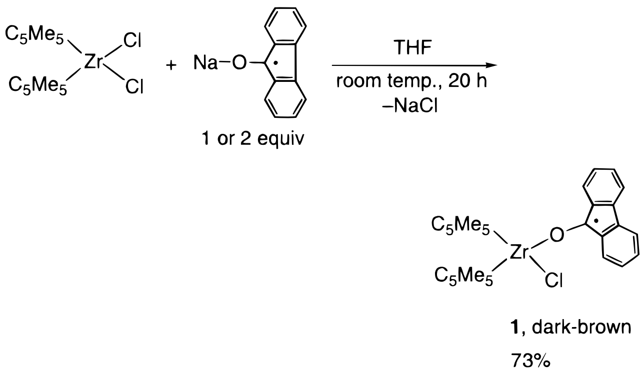
Scheme 1



characterized d-block transition-metal ketyl complex, $(C_5Me_5)_2Zr(OC_{13}H_8)Cl$, which is synthesized by the metathesis reaction of sodium fluorenone ketyl with $(C_5Me_5)_2ZrCl_2$. Similar approaches to iridium ketyl, the reactions of alkali metals with an iridium chloride/hydride complex, and deprotonation of pinacols with an iridium imido complex are also described. Dramatic metal dependence of the reactivity of the ketyl species has been observed.

Results and Discussion

Reaction of Sodium Fluorenone Ketyl with $(C_5Me_5)_2ZrCl_2$. As a typical example of nonreducing early-transition-metal compounds, the Zr(IV) complex $(C_5Me_5)_2ZrCl_2$ was first chosen. Reaction of $(C_5Me_5)_2ZrCl_2$ with 1 equiv of sodium fluorenone ketyl in THF[9] was carried out according to Scheme 1. From this reaction the dark brown crystalline product **1** was isolated in 73% yield. The ESR spectrum of **1** in THF ($g = 2.0032$) was very similar to that of sodium fluorenone ketyl and those of other metal fluorenone ketyl species,[4,8,9,11] suggesting that **1** contains a ketyl radical species. The UV–vis spectrum of **1** showed a maximum absorbance at 415 nm, which was greatly blue-shifted from that of the starting sodium fluorenone ketyl (see Figure 1). This result suggested that transfer of fluorenone ketyl from sodium to the zirconium metal center had occurred.[14]

Single crystals suitable for diffraction studies were obtained by recrystallization of **1** from toluene/OEt_2. An X-ray analysis has revealed that **1** is a zirconium(IV) fluorenone ketyl complex which is stabilized by two C_5Me_5 and one Cl ligands (Figure 2 and Table 1). The length of the C–O bond in the fluorenone ketyl unit of **1** (1.315(8) Å) is in the 1.27–1.32 Å range reported for other metal ketyl complexes.[3–11] The distance is longer than the C–O double bond of free fluorenone (1.220(4) Å)[15] but shorter than the C–O single bond found in the fluorenoxide ligand of $Sm(OC_{13}H_9)(OAr)_2(HMPA)_2$ (1.404(8) Å; Ar = $C_6H_2{}^tBu_2$-2,6-Me-4, HMPA = hexamethylphosphoric triamide).[16] The Zr–O(ketyl) bond distance

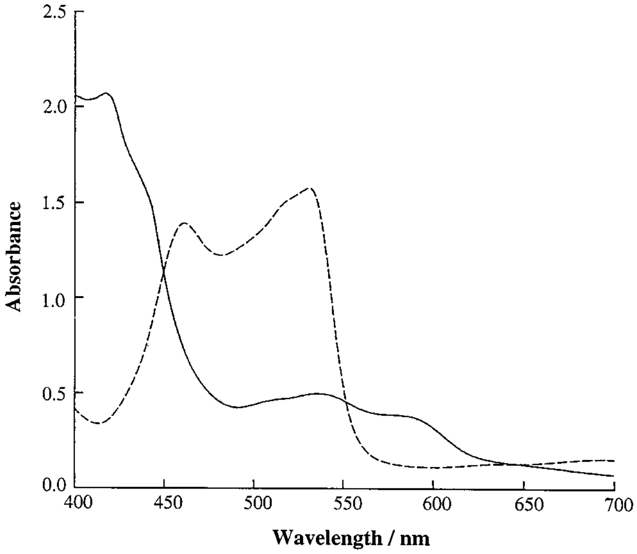


Figure 1. UV–vis spectra in THF: (solid line) Zr ketyl complex **1** (5.54×10^{-4} mmol/cm^3): (dashed line) sodium fluorenone ketyl (5.43×10^{-4} mmol/cm^3).

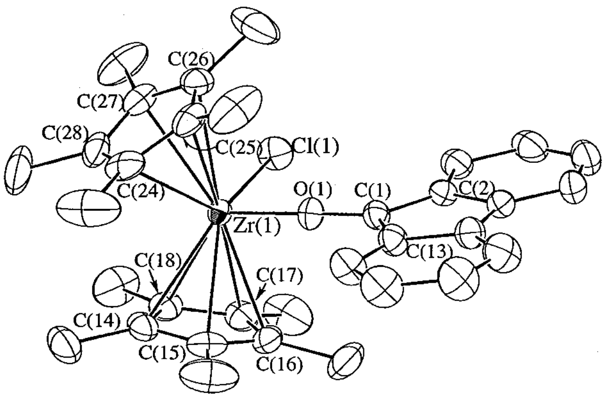


Figure 2. ORTEP drawing of **1** with 30% thermal ellipsoids. The lattice solvent is omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of 1

Zr(1)–Cl(1)	2.456(2)	Zr(1)–O(1)	2.002(5)
Zr(1)–C(14)	2.562(7)	Zr(1)–C(15)	2.523(8)
Zr(1)–C(16)	2.554(7)	Zr(1)–C(17)	2.561(7)
Zr(1)–C(18)	2.539(7)	Zr(1)–C(24)	2.540(7)
Zr(1)–C(25)	2.562(7)	Zr(1)–C(26)	2.544(7)
Zr(1)–C(27)	2.564(6)	Zr(1)–C(28)	2.553(7)
O(1)–C(1)	1.315(8)		

Cp*(centroid)–Zr(1)–Cp*(centroid)	137.4
O(1)–Zr(1)–Cp*$_{C(14)-C(18)}$(centroid)	104.9
O(1)–Zr(1)–Cp*$_{C(24)-C(28)}$(centroid)	105.2
Cl(1)–Zr(1)–Cp*$_{C(14)-C(18)}$(centroid)	103.7
Cl(1)–Zr(1)–Cp*$_{C(24)-C(28)}$(centroid)	101.8

Cl(1)–Zr(1)–O(1)	97.0(2)	Zr(1)–O(1)–C(1)	170.4(4)
O(1)–C(1)–C(2)	124.9(6)	O(1)–C(1)–C(13)	126.1(6)
C(2)–C(1)–C(13)	108.9(6)		

in **1** (2.002(5) Å) can be compared with those of the Zr–OH and Zr–OAr bonds found in $(C_5Me_5)_2Zr(OH)Cl$ (1.950(2) Å),[17] $(C_5Me_5)_2Zr(OH)_2$ (1.975(2), 1.982(7) Å),[17] $Zr(OAr)_2(\eta^2\text{-}^tBuNCCH_2Ph)_2$ (2.027(2) Å),[18] and Zr(OAr)-

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[14] Metal dependence of the λ_{max} value of ketyls in UV–vis spectra has been previously observed. See: (a) Mao, S. W.; Hirota, N. *Chem. Phys. Lett.* **1973**, *22*, 26. (b) Mao, S. W.; Nakamura, K.; Hirota, N. *J. Am. Chem. Soc.* **1974**, *96*, 5341. See also refs 4 and 10.

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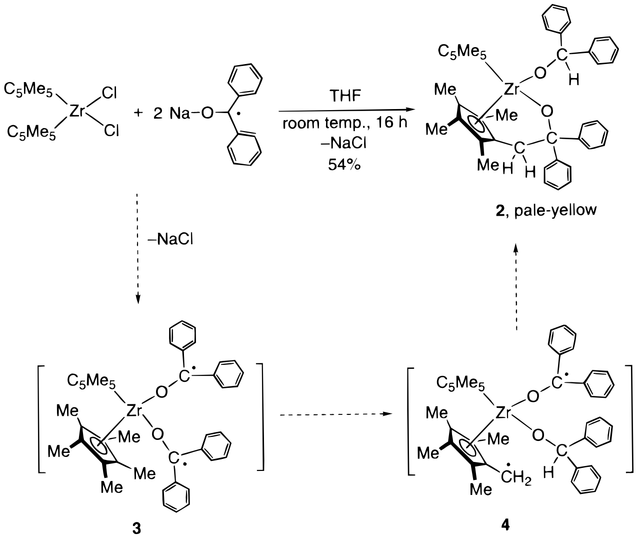
Scheme 2



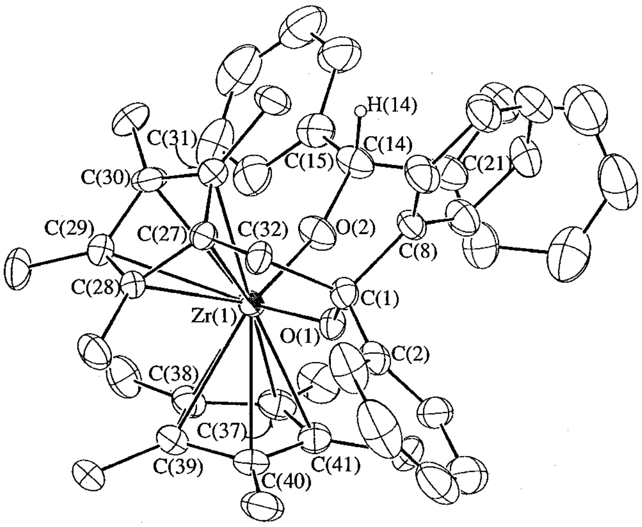


Figure 3. ORTEP drawing of **2** with 30% thermal ellipsoids.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of 2

Zr(1)−O(1)	2.015(7)	Zr(1)−O(2)	1.983(8)
Zr(1)−C(27)	2.501(10)	Zr(1)−C(28)	2.563(10)
Zr(1)−C(29)	2.620(11)	Zr(1)−C(30)	2.624(12)
Zr(1)−C(31)	2.545(12)	Zr(1)−C(37)	2.653(13)
Zr(1)−C(38)	2.621(12)	Zr(1)−C(39)	2.618(12)
Zr(1)−C(40)	2.588(11)	Zr(1)−C(41)	2.580(13)
O(1)−C(1)	1.402(13)	O(2)−C(14)	1.409(14)
C(1)−C(32)	1.573(15)	C(27)−C(32)	1.506(16)
C(14)−H(14)	1.02(16)		
Cp*(centroid)−Zr(1)−Cp′(centroid)	134.1		
O(1)−Zr(1)−Cp*(centroid)	103.4		
O(1)−Zr(1)−Cp′(centroid)	97.9		
O(2)−Zr(1)−Cp*(centroid)	106.3		
O(2)−Zr(1)−Cp′(centroid)	108.4		
O(1)−Zr(1)−O(2)	101.7(4)	Zr(1)−O(1)−C(1)	135.4(7)
Zr(1)−O(2)−C(14)	158.4(8)	O(1)−C(1)−C(2)	111.1(10)
O(1)−C(1)−C(8)	109.7(9)	O(1)−C(1)−C(32)	107.7(9)
C(2)−C(1)−C(8)	107.1(9)	C(2)−C(1)−C(32)	111.2(10)
C(8)−C(1)−C(32)	110.0(9)	O(2)−C(14)−C(15)	113.1(11)
O(2)−C(14)−C(21)	111.9(10)	C(15)−C(14)−C(21)	111.0(10)
C(1)−C(32)−C(27)	110.9(9)		

(η^2-^{t}BuNCCH$_2$Ph)$_3$ (2.058(2) Å) (Ar = C$_6$H$_3$^{t}Bu$_2$-2,6).[18,19] Similar to the case for other fluorenone ketyl complexes,[4,8−11] the whole fluorenone ketyl unit of **1** remains planar, showing that the radical carbon atom in the ketyl unit is still in an sp^2 hybrid state.

Further reaction of the mono(ketyl)zirconium chloride complex with 1 equiv of sodium fluorenone ketyl to give a bis(ketyl)zirconium species was not observed in THF at room temperature, probably due to steric hindrance. Similarly, the reaction of $(C_5Me_5)_2ZrCl_2$ with 2 equiv of sodium fluorenone ketyl under the same conditions gave **1** as the only isolable zirconium species. As far as we are aware, complex **1** represents the first example of a structurally characterized d-block transition-metal ketyl complex.

Reaction of Sodium Benzophenone Ketyl with $(C_5Me_5)_2ZrCl_2$. Next, the reaction of $(C_5Me_5)_2ZrCl_2$ with 2 equiv of sodium benzophenone ketyl was carried out. A color change from blue to purple-red was observed during the reaction. However, in contrast to what was observed in the case of fluorenone ketyl, the color of the reaction mixture faded gradually overnight, and an ESR-silent pale yellow crystalline product (**2**) was finally obtained (Scheme 2) in 54% yield.

An X-ray analysis has shown that **2** is a zirconium(IV) complex which contains a C_5Me_5 ligand and two benzophenone-derived units, one of which is coupled with a $C_5Me_4CH_2$ unit through its carbonyl carbon atom, while the other is hydrogenated at the carbonyl carbon atom to form a normal diphenylmethoxide ligand (Figure 3, Table 2). The ^{1}H NMR spectrum of **2** in CD_2Cl_2 is consistent with its solid-state structure. The $C_5Me_4CH_2$ unit shows four singlets for the Me groups at δ 2.09, 2.02, 1.36, and 1.28, respectively, and two doublets (J = 14 Hz) for the CH$_2$ group at δ 3.75 and 3.64, respectively. Well-resolved signals for the phenyl groups are observed in the range δ 7.61−6.65, while the OCH part in the diphenylmethoxide unit appears as a singlet at δ 6.22. The C_5Me_5 group gives a singlet at δ 1.94.

The formation of **2** could be explained by the reaction paths shown in Scheme 2. The reaction of $(C_5Me_5)_2ZrCl_2$ with 2 equiv of sodium benzophenone ketyl could first give the bis(ketyl) species **3**. The initial color change of the reaction mixture from blue (sodium benzophenone ketyl) to purple-red is consistent with the formation of a zirconium ketyl species at the early stages of the reaction. Abstraction of a hydrogen atom (H$^\bullet$) from a C_5Me_5 group by one of the two benzophenone ketyls in **3** would afford **4**, and then intramolecular coupling between the other benzophenone ketyl radical and the resulting $C_5Me_4CH_2^\bullet$ radical could produce **2**.

The isolation of **2** rather than a benzophenone ketyl species in the present reaction again demonstrates that benzophenone ketyl is more reactive than fluorenone ketyl due to its less conjugated structure.[6] In the case of **1** or the previously reported C_5Me_5-ligated lanthanide fluorenone ketyl complexes,[4] hydrogen abstraction from a C_5Me_5 group by fluorenone ketyl was not observed.

Reactions of Sodium Ketyls with $[(C_5Me_5)Ir(\mu\text{-}Cl)Cl]_2$. To see how a ketyl radical species would interact with a late-transition-metal center, the reaction of the iridium(III) dichloride complex $[(C_5Me_5)Ir(\mu\text{-}Cl)Cl]_2$ with 4 equiv of sodium fluorenone ketyl in THF was carried out (Scheme 3). Unexpectedly, the decarbony-

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[19] The similarity in bond distances between metal−ketyl bonds and metal−aryloxide bonds has been previously observed.[4]

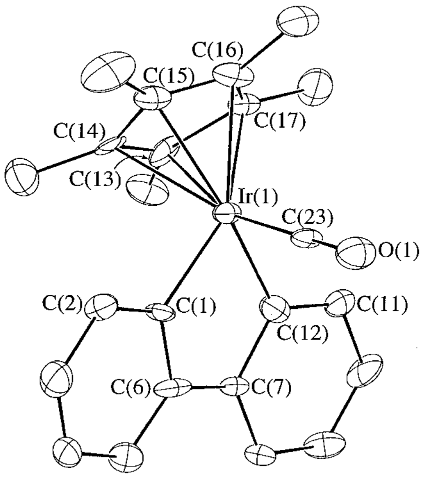


Figure 4. ORTEP drawing of **5** with 30% thermal ellipsoids. Only one of the two independent molecules is shown for clarity.

Scheme 3

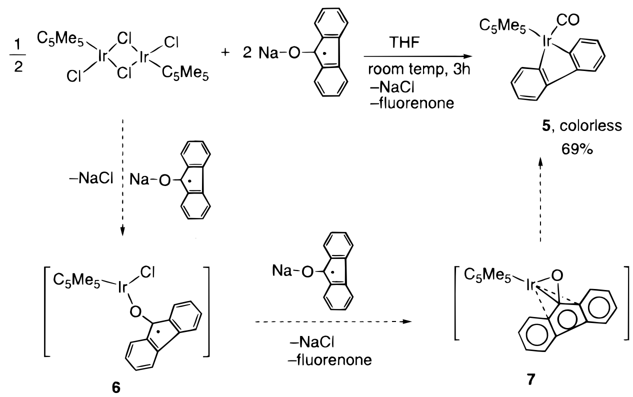
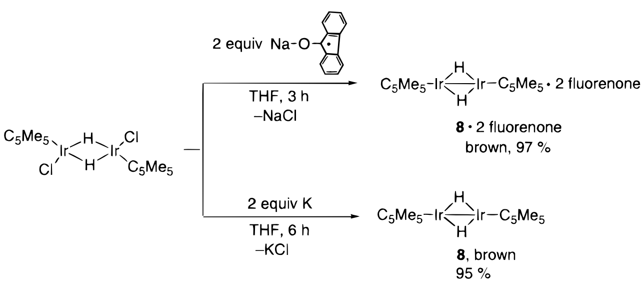


Table 3. Selected Bond Lengths (Å) and Angles (deg) of 5

Ir(1)–C(1)	2.07(2)	Ir(1)–C(12)	2.05(2)
Ir(1)–C(13)	2.25(3)	Ir(1)–C(14)	2.27(3)
Ir(1)–C(15)	2.27(3)	Ir(1)–C(16)	2.27(2)
Ir(1)–C(17)	2.28(2)	Ir(1)–C(23)	1.83(1)
O(1)–C(23)	1.14(3)		
C(1)–Ir(1)–Cp*(centroid)	126.5		
C(12)–Ir(1)–Cp*(centroid)	126.1		
C(23)–Ir(1)–Cp*(centroid)	135.4		
C(1)–Ir(1)–C(12)	77.7(8)	C(1)–Ir(1)–C(23)	86.4(8)
C(12)–Ir(1)–C(23)	86.0(9)	Ir(1)–C(23)–O(1)	179(2)

lation product **5** together with free fluorenone was obtained in this reaction (Figure 4, Table 3).[20] The reaction of [(C$_5$Me$_5$)Ir(μ-Cl)Cl]$_2$ with 2 equiv of sodium fluorenone dianion also gave **5**, but without the formation of fluorenone.[20] To obtain **5**, the prior preparation of sodium fluorenone ketyl or fluorenone dianion is not required. The one-pot reaction of [(C$_5$Me$_5$)Ir(μ-Cl)Cl]$_2$ with 4 equiv of sodium and 2 equiv of fluorenone in THF also afforded **5** in about 70% isolated yield. However, if the reaction was carried out by first mixing [(C$_5$Me$_5$)-Ir(μ-Cl)Cl]$_2$ with sodium for a few hours and then adding fluorenone, a mixture of unidentified iridium hydrides was formed, while fluorenone remained unchanged. No reaction was observed between the Ir(I) complex (C$_5$Me$_5$)Ir(CH$_2$CH$_2$)$_2$[21] and fluorenone at either room temperature or 60 °C in THF. These results suggest that the formation of **5** is mediated by an iridium fluorenone ketyl or fluorenone dianion species. One possible mechanism for the formation of **5** is shown in Scheme 3.[20]

Scheme 4



The formation of **5** under the present reaction conditions constitutes a rare example of room-temperature decarbonylation of a ketone moiety. Although the C–C bond cleavage of cyclic ketones by low-valent transition metals has been known for a long time,[22,23] the decarbonylation of fluorenone is, to the best of our knowledge, unprecedented.

The similar reaction of [(C$_5$Me$_5$)Ir(μ-Cl)Cl]$_2$ with sodium benzophenone ketyl yielded a mixture of unidentified iridium hydrides and benzophenone. Neither an iridium benzophenone ketyl species nor the decarbonylation product was observed, which again demonstrates that benzophenone ketyl behaves differently from fluorenone ketyl.

Reactions of Sodium Fluorenone Ketyl and Alkali Metals with [(C$_5$Me$_5$)Ir(μ-H)Cl]$_2$. In an attempt to obtain a better understanding of the decarbonylation of fluorenone ketyl in its reaction with the iridium(III) dichloride complex [(C$_5$Me$_5$)Ir(μ-Cl)Cl]$_2$, the similar reaction of the iridium(III) chloride/hydride complex [(C$_5$Me$_5$)Ir(μ-H)Cl]$_2$ with 2 equiv of sodium fluorenone ketyl was carried out (Scheme 4). In this reaction, formation of a fluorenone decarbonylation product was not observed, but instead, the reduction (dechlorination) of the iridium(III) chloride/hydride complex took place to give the corresponding iridium(II) hydride complex [(C$_5$Me$_5$)Ir(μ-H)]$_2$ (**8**) and fluorenone almost quantitatively. The similar reaction of [(C$_5$Me$_5$)-Ir(μ-H)Cl]$_2$ with sodium benzophenone ketyl gave **8** and benzophenone almost quantitatively. The ketone-free **8** was isolated as fine brown crystals in 95% yield from the reaction of [(C$_5$Me$_5$)Ir(μ-H)Cl]$_2$ with 2 equiv of K in THF (Scheme 4). Similarly, the reaction of [(C$_5$Me$_5$)Ir-(μ-H)Cl]$_2$ with Na also produced **8**, but a longer reaction time (2 days) was required to complete the reaction.

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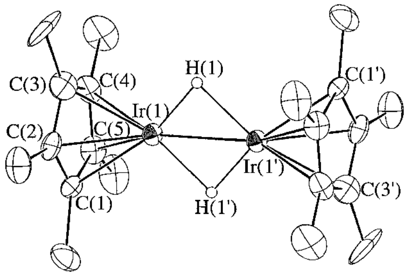

Figure 5. ORTEP drawing of **8** with 30% thermal ellipsoids. Fluorenone is omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) of 8

Ir(1)−Ir(1′)	2.4157(6)	Ir(1)−C(1)	2.187(11)
Ir(1)−C(2)	2.215(14)	Ir(1)−C(3)	2.18(3)
Ir(1)−C(4)	2.216(16)	Ir(1)−C(5)	2.222(13)
Ir(1)−H(1)	1.61	Ir(1)−H(1′)	1.80

Cp*(centroid)−Ir(1)−Ir(1′)	179
Cp*(centroid)−Ir(1)−H(1)	133
Cp*(centroid)−Ir(1)−H(1′)	137
H(1)−Ir(1)−H(1′)	90.2
Ir(1)−H(1)−Ir(1′)	89.8

The ^{1}H NMR spectrum of **8** in C_6D_6 showed a singlet at δ 1.81 for the C_5Me_5 groups and a singlet at δ −13.42 for the hydrides.[24] Crystals suitable for diffraction studies were obtained in the form of **8**·2(fluorenone) from benzene. An X-ray analysis has established that **8** is a dihydride-bridged binuclear iridium(II) complex which possesses a crystallographic inversion center at the center of the molecule (Figure 5, Table 4). The length of the Ir(1)−Ir(1′) bond in **8** (2.4157(6) Å) is much shorter than those previously reported for the formal Ir−Ir triple bonds found in the cationic complexes $[(C_5Me_5)_2Ir_2(\mu\text{-}H)_3]^+[BF_4]^-$ (2.458(6) Å),[25] $[Ir_2(\mu\text{-}H)_3H_2(PPh_3)_4]^+[PF_6]^-$ (2.518 Å),[26] and $[Ir_2H_5(dppp)_2]^+[BF_4]^-$ (2.514(1) Å) (dppp = 1,3-bis(diphenylphosphino)propane)[27] and those for the formal Ir−Ir double bonds found in $[(C_5Me_5)Ir(\mu\text{-}CO)]_2$ (2.554(1) Å)[28] and $[Ir(\mu\text{-}PPh_2)(CO)(PPh_3)]_2$ (2.551(1) Å).[29] To the best of our knowledge, the Ir(1)−Ir(1′) bond distance in **8** is the shortest ever reported for a bonding interaction between iridium atoms. Although this unusually short Ir−Ir bond distance and the 18-electron rule may suggest that **8** should possess an Ir−Ir triple bond, an examination of the molecular orbitals has shown that only a single metal−metal bond may be formed between the two Ir atoms, which is similar to the situation of the isoelectronic tetrahydride-bridged Ru complex $(C_5Me_5)Ru(\mu\text{-}H)_4Ru(C_5Me_5)$.[30,31]

Reactions of $(C_5Me_5)IrN^tBu$ with Aromatic Pinacols. Parallel to the metathesis approaches described above, an attempt to generate an iridium ketyl species via deprotonation of a pinacol and subsequent C−C bond cleavage of the resulting pinacolate was also made.[4,9] The reaction of 1,2-bis(biphenyl-2,2′-diyl)ethane-1,2-diol (**9**) with the iridium(III) imido complex $(C_5Me_5)IrN^tBu$ in THF gave the iridium(III) carbonyl complex **5** and the iridium(II) hydride complex **8**·2(fluorenone) in 30% isolated yield, respectively, as confirmed by ^{1}H NMR and X-ray analyses (Scheme 5). However, when the reaction was carried out in benzene, the pinacolate complex **10** was formed as a major product (73%) together with a small amount of **5** (9%) and **8** (13%). Purple-brown crystals of **10** suitable for X-ray analyses were obtained from THF/OEt_2/hexane. An ORTEP drawing and selected bond lengths and angles for **10** are given in Figure 6 and Table 5, respectively. Complex **10** represents a rare example of a structurally characterized iridium pinacolate complex. The similar reaction of benzopinacol with $(C_5Me_5)IrN^tBu$ in THF yielded benzophenone and several unidentified species.

Table 5. Selected Bond Lengths (Å) and Angles (deg) of 10

Ir(1)−O(1)	1.963(6)	Ir(1)−O(2)	1.977(7)
Ir(1)−C(27)	2.129(9)	Ir(1)−C(28)	2.154(9)
Ir(1)−C(29)	2.130(11)	Ir(1)−C(30)	2.130(11)
Ir(1)−C(31)	2.138(9)	O(1)−C(1)	1.428(10)
O(2)−C(14)	1.419(11)	C(1)−C(14)	1.567(12)

O(1)−Ir(1)−Cp*(centroid)	138.7
O(2)−Ir(1)−Cp*(centroid)	139.4
O(1)−Ir(1)−O(2)	81.9(3)
Ir(1)−O(1)−C(1)	113.8(5)
Ir(1)−O(2)−C(14)	113.0(5)

The formation of **10** could be viewed as a simple proton-exchange reaction between the pinacol **9** and the iridium imido complex $(C_5Me_5)IrN^tBu$, while the routes to **5** and **8**·2(fluorenone) are not so straightforward. Apparently, formation of **5** and **8**·2(fluorenone) requires the cleavage of the central C−C bond of the pinacol **9**. As in the case of the metathesis reactions described above, an iridium ketyl species might possibly be formed as an intermediate,[4,9] although details including the solvent effects are not yet clear. Conversion of the pinacolate **10** to either **5** or **8**·2(fluorenone) was not observed in THF at either room or reflux temperature.

Concluding Remarks

We have demonstrated that the metathesis reaction of alkali-metal ketyls with d-block transition-metal chlorides can be a convenient method for the preparation of the corresponding transition-metal ketyls. However, the isolability or reactivity of the resulting transition-metal ketyls depends significantly on both the nature of the metal centers and the structure of the ketyl species. The zirconium fluorenone ketyl complex **1** was successfully isolated from the reaction of $(C_5Me_5)_2ZrCl_2$ with sodium fluorenone ketyl, while in the case of benzophenone ketyl further reaction between the ketyl radical and the C_5Me_5 ligand took place to give finally the zirconium bis(alkoxide) complex **2**. In contrast, the similar reaction of $[(C_5Me_5)Ir(\mu\text{-}Cl)Cl]_2$ with sodium fluorenone ketyl yielded the iridium carbonyl complex **5**, as a result of decarbonylation of fluorenone. This demonstrates that late transition metals may

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[24] The ^{1}H NMR signals for the starting iridium(III) chloride/hydride complex $[(C_5Me_5)Ir(\mu\text{-}H)Cl]_2$ are at δ 1.51 for C_5Me_5 and δ −13.48 for Ir−H, respectively.

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Scheme 5

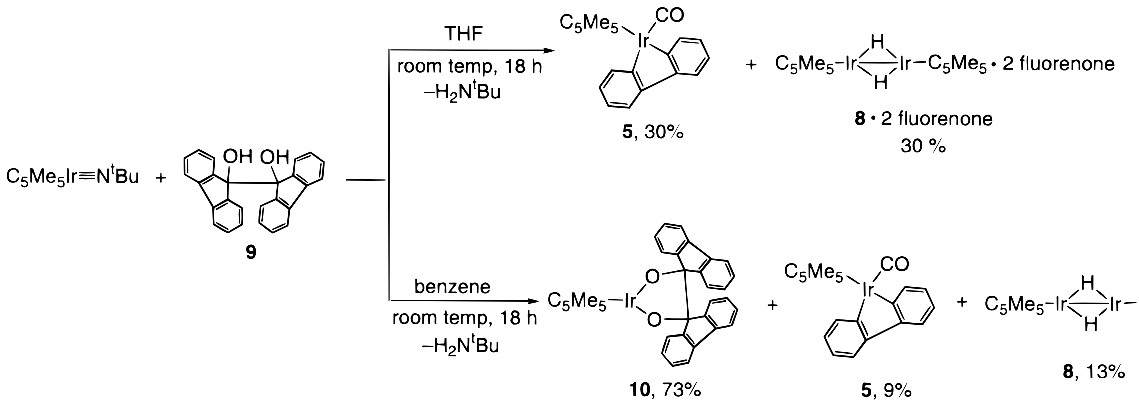

Table 6. Summary of Crystallographic Data

	1·THF	**2**	[**5**]$_2$	**8**·2(fluorenone)	**10**·0.5C_6H_{14}
formula	$C_{37}H_{46}O_2ClZr$	$C_{46}H_{50}O_2Zr$	$C_{46}H_{46}O_2Ir_2$	$C_{46}H_{48}O_2Ir_2$	$C_{39}H_{38}O_2Ir$
fw	649.45	726.13	1015.32	1017.33	730.96
cryst syst	monoclinic	triclinic	orthorhombic	triclinic	triclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	*Pcab* (No. 61)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	19.012(7)	9.869(2)	16.476(5)	8.722(4)	11.204(6)
b (Å)	9.637(5)	11.435(4)	31.468(8)	10.571(2)	11.618(9)
c (Å)	18.277(7)	17.399(5)	14.645(4)	11.778(2)	12.542(4)
α (deg)		104.72(3)		104.01(2)	104.57(5)
β (deg)	95.55(3)	92.25(2)		96.89(2)	92.09(4)
γ (deg)		100.04(2)		66.67(2)	83.23(6)
V (Å^3)	3333(2)	1862.7(9)	7593(3)	968.0(5)	1569(2)
Z	4	2	8	1	2
D_{calcd} (g cm^{-3})	1.29	1.29	1.78	1.75	1.55
radiation, *λ* (Å)	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73
data collcd	$+h,+k,\pm l$	$\pm h,+k,\pm l$	$+h,+k,+l$	$-h,\pm k,\pm l$	$\pm h,-k,\pm l$
scan speed (deg/min)	6	6	6	6	6
2*θ* range (deg)	3−55	3−50	3−55	3−55	3−55
μ (cm^{-1})	3.486	3.245	70.131	68.766	42.691
no. of rflns collcd	8612	7143	9831	5090	7802
no. of unique rflns	6661	5648	7404	4438	6671
no. of rflns with $I_o > 3\sigma(I_o)$	5165	3183	4071	4010	5386
no. of variables	370	446	451	230	364
R_{int}	0.04	0.05		0.03	0.03
R (%)	6.00	6.70	5.76	7.38	5.67
R_w (%)	7.71	8.65	6.93	8.72	7.22

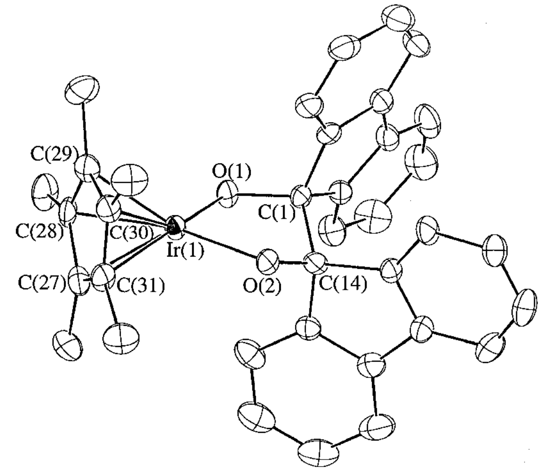

Figure 6. ORTEP drawing of **10** with 30% thermal ellipsoids. The lattice solvent is omitted for clarity.

behave very differently toward alkali-metal ketyls than early transition metals. When [$(C_5Me_5)Ir(\mu\text{-}H)Cl]_2$ was used, the dechlorination (reduction) product [$(C_5Me_5)Ir(\mu\text{-}H)]_2$ (**8**) formed selectively, showing that a subtle change in the environment around the metal center can greatly alter the behavior of a ketyl species. In view of the dramatic metal dependence of the reactivity of the ketyl species and the great variety of transition-metal compounds, a very rich chemistry for transition-metal ketyls can be expected.

Experimental Section

General Methods. All manipulations were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an Mbraun glovebox. The argon was purified by passing through a Dryclean column (4A molecular sieves, Nikka Seiko Co.) and a Gasclean GC-XR column (Nikka Seiko Co.). The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves (4A) catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi-Analyzer (Mbraun) to ensure both were always below 1 ppm. Samples for spectroscopic studies were prepared in the glovebox. J. Young valve UV cells and NMR tubes (Wilmad 528-JY) were used for measurements. UV−vis spectra were recorded on a Shimadzu UV-2400PC spectrometer. ESR spectra were obtained on a JEOL JES FE 3AX X-band spectrometer, and the *g* value was calibrated with DPPH (2,2-diphenyl-1-picrylhydrazyl). ^1H NMR spectra were recorded on a JNM-EX 270 (FT, 270 MHz) spectrometer and are reported in ppm downfield from tetramethylsilane. Elemental analyses were performed by the chemical analysis laboratory of The Institute of Physical and Chemical Research (RIKEN). Solvents were distilled from sodium/benzophenone ketyl, degassed by the freeze−thaw method (three times), and dried over fresh Na chips in the glovebox. $(C_5Me_5)_2ZrCl_2$ and

$[(C_5Me_5)Ir(\mu\text{-}Cl)Cl]_2$ were purchased from Aldrich. $(C_5Me_5)IrN^tBu$[32] and $[(C_5Me_5)Ir(\mu\text{-}H)Cl]_2$[33] were synthesized according to the literature. Sodium ketyls were synthesized by the reactions of sodium metal with 1 equiv of ketones in THF[9] and were used for subsequent reactions without isolation.

$(C_5Me_5)_2Zr(OC_{13}H_8)Cl$ (1). Addition of a brown THF solution (10 mL) of sodium fluorenone ketyl (0.44 mmol) to $(C_5Me_5)_2ZrCl_2$ (188 mg, 0.44 mmol) in THF (10 mL) gave gradually a dark brown mixture, which was stirred at room temperature for 20 h. After removal of NaCl by filtration, the THF solvent was pumped off to give a dark brown crystalline product, which after recrystallization from toluene/OEt_2 yielded **1** as dark brown blocks (185 mg, 0.32 mmol, 73% yield). The similar reaction of $(C_5Me_5)_2ZrCl_2$ with 2 equiv of sodium fluorenone ketyl also gave **1** as the only isolable zirconium species. Formation of a bis(ketyl)zirconium species was not observed. The UV−vis spectrum of **1** is shown in Figure 1. ESR (THF, 22 °C): $g = 2.0032$. Anal. Calcd for $C_{33}H_{38}OClZr$: C, 68.65; H, 6.63. Found: C, 67.75; H, 6.50.

$(\eta^5\text{-}C_5Me_5)(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2C(Ph)_2O)Zr(OCHPh_2)$ (2). Addition of a blue THF solution (10 mL) of sodium benzophenone ketyl (0.44 mmol) to $(C_5Me_5)_2ZrCl_2$ (94 mg, 0.22 mmol) in THF (10 mL) gave gradually a purple-red mixture whose color eventually faded when being stirred at room temperature for 16 h. After removal of NaCl by filtration, the THF solvent was pumped off to give a yellow residue, which was then dissolved in toluene and concentrated. Addition of OEt_2 gave **2** as pale yellow blocks (85 mg, 0.12 mmol, 54% yield). ^{1}H NMR (CD_2Cl_2, 22 °C): δ 7.61 (d, $J = 8.41$ Hz, 2 H, Ph), 7.21−7.47 (m, 14 H, Ph), 7.10 (t, $J = 7.26$ Hz, 1 H, Ph), 6.85 (t, $J = 7.26$ Hz, 1 H, Ph), 6.65 (t, $J = 7.59$ Hz, 2 H, Ph), 6.22 (s, 1 H, $OC\mathit{H}Ph_2$), 3.75 (d, $J = 14$ Hz, 1 H, $C_5Me_4C\mathit{H}_2$), 3.64 (d, $J = 14$ Hz, 1 H, $C_5Me_4C\mathit{H}_2$), 2.09 (s, 3 H, $C_5\mathit{Me}_4CH_2$), 2.02 (s, 3 H, $C_5\mathit{Me}_4CH_2$), 1.36 (s, 3 H, $C_5\mathit{Me}_4CH_2$), 1.28 (s, 3 H, $C_5\mathit{Me}_4CH_2$), 1.94 (s, 15 H, C_5Me_5). ^{13}C NMR (CD_2Cl_2, 22 °C): δ 154.1, 154.0, 147.7, 147.3, 136.1, 128.0, 127.9, 127.8, 127.7, 127.6, 126.8, 126.7, 126.1, 125.9, 125.4, 125.2, 122.0, 120.6, 119.6, 117.1, 114.7, 106.6, 82.4, 39.4, 12.0, 11.7, 11.1, 10.9. Anal. Calcd for $C_{46}H_{50}O_2Zr$: C, 76.09; H, 6.94. Found: C, 75.81; H, 6.85.

$(C_5Me_5)Ir(CO)(C_{12}H_8)$ (5). A brown THF solution (10 mL) of sodium fluorenone ketyl (0.44 mmol) was added to $[(C_5Me_5)Ir(\mu\text{-}Cl)Cl]_2$ (87 mg, 0.11 mmol) in THF (10 mL). The resulting brown mixture was stirred at room temperature for 3 h. After removal of NaCl by filtration, the THF solvent was pumped off to give a light brown residue, which was then dissolved in toluene and concentrated. Addition of OEt_2 gave **5** as colorless blocks (77 mg, 0.15 mmol, 69% yield). Fluorenone was confirmed in the mother liquor by ^{1}H NMR comparison with an authentic sample. The similar reaction of $[(C_5Me_5)Ir(\mu\text{-}Cl)Cl]_2$ with 2 equiv of sodium fluorenone dianion gave **5** in 68% isolated yield, without the formation of fluorenone being observed.[20] ^{1}H NMR (CD_2Cl_2, 22 °C): δ 7.47 (d of d, $J_1 = 7.26$ Hz, $J_2 = 1.32$ Hz, 2 H, $C_{12}H_8$), 7.46 (d of d, $J_1 = 7.26$ Hz, $J_2 = 1.32$ Hz, 2 H, $C_{12}H_8$), 7.06 (d of t, $J_1 = 7.26$ Hz, $J_2 = 1.32$ Hz, 2 H, $C_{12}H_8$), 6.90 (d of t, $J_1 = 7.26$ Hz, $J_2 = 1.32$ Hz, 2 H, $C_{12}H_8$), 1.87 (s, 15 H, C_5Me_5). ^{13}C NMR (CD_2Cl_2, 22 °C): δ 169.3, 154.5, 141.1, 137.2, 125.8, 123.6, 120.3, 99.1, 8.8. IR (in THF): ν(CO) 1996.9 cm^{-1}. Anal. Calcd for $C_{23}H_{23}OIr$: C, 54.42; H, 4.57. Found: C, 54.24, H, 4.49.

$[(C_5Me_5)Ir(\mu\text{-}H)]_2$ (8). A blue THF solution (10 mL) of $[(C_5Me_5)Ir(\mu\text{-}H)Cl]_2$ (364 mg, 0.5 mmol) was added to freshly cut K chips (39 mg, 1.0 mmol). The mixture was stirred at room temperature for 6 h, during which time the color changed gradually from blue to brown. After removal of KCl by filtration, the solution was concentrated under reduced pressure. Addition of hexane gave **8** as a brown powder (312 mg, 0.475 mmol, 95% yield). The similar reaction of $[(C_5Me_5)Ir(\mu\text{-}H)Cl]_2$ with Na also yielded **8**, but a longer reaction time (2 days) was required to complete the reaction. Reaction of $[(C_5Me_5)Ir(\mu\text{-}H)Cl]_2$ with 2 equiv of sodium fluorenone ketyl in THF for 3 h yielded, after recrystallization from benzene, brown crystals of **8**·2(fluorenone) (97% yield), which were suitable for diffraction studies. ^{1}H NMR for **8** (C_6D_6, 22 °C): δ 1.81 (s, 30 H, C_5Me_5), −13.42 (s, 2 H, Ir−H). ^{13}C NMR (C_6D_6, 22 °C): δ 85.8, 11.7. Anal. Calcd for $C_{20}H_{32}Ir_2$: C, 36.57; H, 4.91. Found: C, 36.42; H, 5.03.

$(C_5Me_5)Ir(O_2C_{26}H_{16})$ (10). Addition of a benzene solution (5 mL) of 1,2-bis(biphenyl-2,2′-diyl)ethane-1,2-diol (**9**; 95 mg, 0.26 mmol) to $(C_5Me_5)IrN^tBu$ (104 mg, 0.26 mmol) in benzene (5 mL) gave a brown solution, which was stirred at room temperature for 18 h. Evaporation of the solvent under vacuum gave a crude brown powder. The ^{1}H NMR spectroscopic study has shown that this crude product is a mixture of **5**, **8**, and **10**, with the yields being 9%, 13%, and 73%, respectively, as measured by using anisole as an internal standard. Purple-brown crystals of **10** suitable for diffraction studies were obtained by recrystallization of the crude brown product from THF/OEt_2/hexane. ^{1}H NMR for **10** (CD_2Cl_2, 22 °C): δ 6.95−7.30 (m, 16 H, $O_2C_{26}H_{16}$), 1.91 (s, 15 H, C_5Me_5). ^{13}C NMR (CD_2Cl_2, 22 °C): δ 139.6, 127.6, 125.8, 125.5, 118.6, 80.5, 9.7. Anal. Calcd for $C_{36}H_{31}O_2Ir$: C, 62.86; H, 4.54. Found: C, 63.12; H, 5.08.

X-ray Crystallographic Studies. Crystals for X-ray analyses were obtained as described in the preparations. The crystals were manipulated in the glovebox under a microscope mounted on the glovebox window and were sealed in thin-walled glass capillaries. Data collections were performed at 20 °C on a Mac Science MXC3K diffractometer (Mo Kα radiation, $\lambda = 0.710\,73$ Å, graphite monochromator, $\omega{-}2\theta$ scan). Lattice constants and orientation matrixes were obtained by least-squares refinement of 22 reflections with $30° \le 2\theta \le 35°$. Three reflections were monitored periodically as a check for crystal decomposition or movement, and no significant decay was observed. All data were corrected for X-ray absorption effects and polarization effects. The observed systematic absences were consistent with the space groups given in Table 6. Structures were solved by direct methods using SIR92 in the Crystan-GM software package. Hydrogen atoms were either located from the difference Fourier maps or placed at the calculated positions. Refinements against $|F|$ were performed anisotropically for non-hydrogen atoms by the block-diagonal least-squares method. Hydrogen atoms were not refined. The function minimized in the least-squares refinements was $\sum(|F_o| - |F_c|)^2$. Neutral atomic scattering factors were taken from ref 34. The residual electron densities were of no chemical significance. Crystal data, data collection, and processing parameters are given in Table 6.

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Supporting Information Available: Listings of atomic coordinates, thermal parameters, and bond distances and angles for **1**, **2**, **5**, **8**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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