Isolation, structure and iridium-mediated decarbonylation of a sodium fluorenone dianion complex

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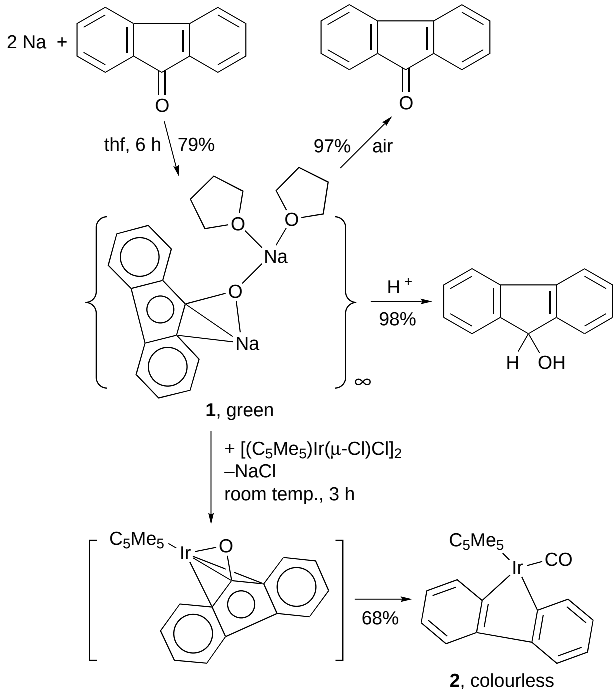
Reaction of fluorenone with 2 equiv. of Na in THF at room temp. gave the polymeric Na–fluorenone dianion complex 1 in 79% isolated yield, which upon reaction with 0.5 equiv. of $[(C_5Me_5)IrCl(\mu\text{-}Cl)]_2$ afforded the decarbonylation product 2; both 1 and 2 have been structurally characterized.

The formation of ketone dianions by two-electron reduction of aromatic ketones with reducing metals such as alkali,[1] low-valent titanium,[2] and lanthanide metals[3] has been known for a long time. These dianionic species as unique nucleophiles have been extensively studied in the area of organic chemistry.[1–3] However, owing to their extreme air- and moisture-sensitivity, which makes them difficult to isolate, structurally characterized examples of this important class of compounds remain very scarce. To date, only two ketone dianion complexes, both of which are limited to those of benzophenone and adopt a dimeric structure, have been isolated and structurally characterized. One is the lithium complex $[Li_2(OCPh_2)(thf)(tmen)]_2$ (thf = tetrahydrofuran, tmen = tetramethylethylenediamine),[4] and the other is the ytterbium(II) complex $[Yb(\mu\text{-}\eta^1:\eta^2\text{-}OCPh_2)(hmpa)_2]_2$ (hmpa = hexamethylphosphoric triamide).[5] Here, we wish to report the isolation and structural characterization of a polymeric sodium fluorenone dianion complex, which constitutes the first example of a structurally characterized fluorenone dianion complex, as well as the first example of a structurally characterized sodium ketone dianion complex. Its reaction with $[(C_5Me_5)IrCl(\mu\text{-}Cl)]_2$ to cause unprecedented decarbonylation of the fluorenone unit is also described.

Reaction of fluorenone with 2 equiv. of fresh sodium chips in thf at room temp. yielded a green precipitate, which upon dissolving in dimethoxyethane (DME) gave a green solution. Evaporation of DME under reduced pressure yielded a green oily residue, which after addition of thf and standing at room temp. for several days afforded green blocks of **1** in 79% yield (Scheme 1).‡ An X-ray analysis has revealed that **1** is a thf-coordinated fluorenonedisodium complex in which one sodium atom [Na(1)] is bonded to the oxygen atom O(1), while the other sodium atom [Na(2)] is bonded to the O(1), C(1) and C(2) atoms of the fluorenone unit (Fig. 1).§ The bond distance of the Na(1)–O(1) bond [2.168(6) Å] is in the 2.14–2.39 Å range of the Na–OR bond distances found in $[NaOBu^t]_6$,[6] $[NaOBu^t]_9$,[6] $[Na\{\mu\text{-}OC_6H_2(CF_3)_3\text{-}2,4,6\}(thf)_2]_2$[7] and $[Na(\mu\text{-}OR)(hmpa)_2]_2$ (OR = fluorenone ketyl),[8] while the bond distances of the Na(2)–C(1) [2.644(7) Å] and Na(2)–C(2) [2.921(7) Å] bonds can be compared with those of the Na–η^{3-5}-Cp bonds (2.620–3.044 Å) found in the sodium fluorenide complexes Na(fluorenide)-$[Me_2N(CH_2)_2N(Me)(CH_2)_2NMe_2]$,[9] $[Na(fluorenide)\{Me_2N(CH_2)_3NMe_2\}]_4$,[9] and $[Na(fluorenide)\{Me_2N(CH_2)_2NMe_2\}]_\infty$.[9] These bond distances are consistent with the fact that **1** is a sodium fluorenone dianion species. The intermolecular interactions between the sodium atoms and part of the fluorenyl ring, the carbonyl unit, and the thf ligands in **1** constitute a unique polymeric structure, in which the fluorenone unit is bonded on one side to a Na atom *via* the Na(2)–η^3-O(1)C(1)C(2) (2.348–2.921 Å) interactions and on the other side to two Na atoms *via* the Na(1′)–η^6-C(8–13) (2.725–2.888 Å) and Na(2′)–η^3-O(1)C(1)C(13) (2.340–3.083 Å) interactions (Fig. 1). The carbonyl moiety interacts with the Na(2) and Na(2′) atoms in a μ-η^2-fashion on two opposite sides (dihedral angle between the Na(2)O(1)C(1) and Na(2′)O(1)C(1) planes = 173°), while the C(13) atom is bonded to both Na(1′) and Na(2′) on the same side [Na(1′)–C(13)–Na(2′) 72.2(2)°]. These structural features are in sharp contrast with those observed in the dimeric benzophenone dianion complexes $[Li_2(OCPh_2)(thf)(tmen)]_2$[4] and $[Yb(\mu\text{-}\eta^1:\eta^2\text{-}OCPh_2)(hmpa)_2]_2$,[5] and apparently result from the planar configuration of the fluorenone unit. The formation of thf bridges in **1** is also noteworthy, since only very few precedents, such as $\{Na(\mu\text{-}thf)[(C_5Me_5)Gd(thf)]_2(\mu\text{-}Cl)(\mu_3\text{-}Cl)_2\}_2$[10] and $[K\{\mu\text{-}OC_6H_2(CF_3)_3\text{-}2,4,6\}(thf)_2(\mu\text{-}thf)]_2$,[7] could be found in the literature. The Na(1)–O(2) [2.371(6) Å] and Na(1)–O(3) [2.391(7) Å] bonds are respectively significantly shorter than the Na(2′)–O(2) [2.440(6) Å] and Na(2′)–O(3) [2.606(6) Å] bonds, showing that the thf bridges in the polymeric structure are unsymmetric, and the intramolecular interactions are stronger than the intermolecular ones. Similarly, the intramolecular Na(2)–C(1) [2.644(7) Å] and Na(2)–C(2) [2.921(7) Å] bonds are respectively much shorter than the intermolecular Na(2′)–C(1) [2.775(7) Å] and Na(2′)–C(13) [3.083(7) Å] bonds, though the Na(2)–O(1) bond distance [2.348(6) Å] is similar to that of the Na(2′)–O(1) bond [2.340(6) Å] (Fig. 1). The bond distance of the C–O bond of the fluorenone unit in **1** [1.379(8) Å] is comparable with those of the benzophenone dianion units found in $[Li_2(OCPh_2)(thf)(tmen)]_2$ (1.406 Å)[4] and $[Yb(\mu\text{-}\eta^1:\eta^2\text{-}OCPh_2)(hmpa)_2]_2$ [1.39(6) Å],[5] and significantly longer than those of free fluorenone [1.220(4) Å][11] and fluorenone ketyl (1.27–1.32 Å).[8,12]



Scheme 1

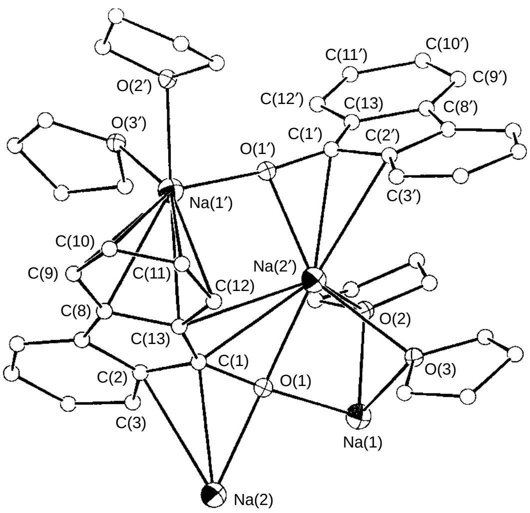


Fig. 1 Extended structure of **1**. Selected bond lengths (Å) angles (°) ($' = 1.5 - x, 0.5 + y, 1.5 - z$): Na(1)–O(1) 2.168(6), Na(1)–O(2) 2.371(6), Na(1)–O(3) 2.391(7), Na(2)–O(1) 2.348(6), Na(2)–C(1) 2.644(7), Na(2)–C(2) 2.921(7), Na(2′)–O(1) 2.340(6), Na(2′)–C(1) 2.775(7), Na(2′)–C(13) 3.083(7), Na(2′)–O(2) 2.440(6), Na(2′)–O(3) 2.606(6), Na(1′)–C(8) 2.733(7), Na(1′)–C(9) 2.822(8), Na(1′)–C(10) 2.888(8), Na(1′)–C(11) 2.881(8), Na(1′)–C(12) 2.805(8), Na(1′)–C(13) 2.725(7), O(1)–C(1) 1.379(8); O(1)–Na(1)–O(2) 91.2(2), O(1)–Na(1)–O(3) 86.2(2), O(2)–Na(1)–O(3) 84.5(3), Na(1)–O(1)–C(1) 164.1(5), Na(2)–O(1)–C(1) 86.3(4), Na(1)–O(1)–Na(2) 98.9(2), Na(1)–O(1)–Na(2′) 83.6(2), Na(2′)–O(1)–C(1) 92.9(4), Na(2)–O(1)–Na(2′) 173.4(3), Na(1′)–C(13)–Na(2′) 72.2(2).

Reflecting the reactivity of a fluorenone dianion species,[1–3] hydrolysis of **1** yielded fluorenol, while air oxidation of **1** afforded fluorenone almost quantitatively. Moreover, when **1** was allowed to react with 0.5 equiv. of $[(C_5Me_5)IrCl(\mu\text{-}Cl)]_2$ at room temp. in DME, the decarbonylation product **2** was obtained as colorless crystals in 68% isolated yield (Scheme 1, Fig. 2).§¶ In contrast, the similar reaction of sodium benzophenone dianion with $[(C_5Me_5)IrCl(\mu\text{-}Cl)]_2$ did not give any C–C bond cleavage product, but instead afforded benzophenone and several unidentified iridium hydride species. These results again demonstrated the difference in behavior between fluorenone dianion and benzophenone dianion. Further studies on the decarbonylation reaction are in progress.

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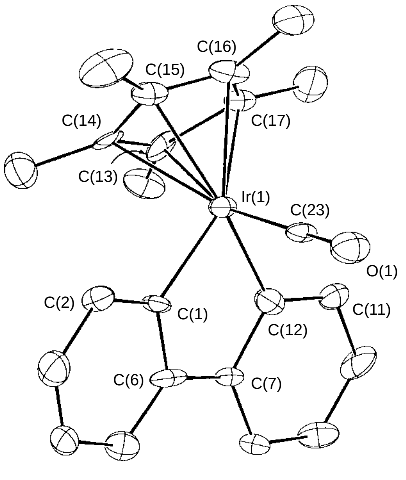

Fig. 2 ORTEP drawing of **2** (only one of the two independent molecules is shown for clarity). Selected bond lengths (Å) and angles (°): Ir(1)–C(1) 2.07(2), Ir(1)–C(12) 2.05(2), Ir(1)–C(13) 2.25(3), Ir(1)–C(14) 2.27(3), Ir(1)–C(15) 2.27(3), Ir(1)–C(16) 2.27(2), Ir(1)–C(17) 2.28(2), Ir(1)–C(23) 1.83(1), O(1)–C(23) 1.14(3); Ir(1)–C(23)–O(1) 179(2).

Notes and References

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‡ A typical procedure for the synthesis of **1** is as follows. In a glove box, addition of a thf solution (5 ml) of fluorenone (180 mg, 1 mmol) to freshly-cut sodium chips (48 mg, 2.1 mmol) gave immediately a brown solution, which after being stirred at room temperature for *ca.* 1 h, changed to dark green and yielded gradually thf-insoluble green precipitates. The green mixture was further stirred at room temperature for 5 h. The thf was pumped off and DME (5 ml) was added to give a green solution. Evaporation of DME yielded a green oily residue, which after addition of thf and standing at room temperature for several days afforded thf-insoluble green blocks of **1** (292 mg, 0.79 mmol, 79% yield). Anal. Calc. for $C_{21}H_{24}Na_2O_3$: C, 68.10; H, 6.53. Found. C, 67.80, H, 6.44%.

§ *Crystal data*: for **1**: $C_{21}H_{24}Na_2O_3$, $M = 370.40$, monoclinic, space group $P2_1/n$ (no. 15), $a = 12.6600(9)$, $b = 8.5523(5)$, $c = 17.8251(11)$ Å, $\beta = 98.942(6)$°, $U = 1906.5(2)$ Å^3, $Z = 4$, $D_c = 1.25$ g cm^{-3}, μ(Cu-Kα) = 10.440 cm^{-1}, 3120 measured reflections, 2892 independent, $R = 0.0847$ ($R_w = 0.0830$) for 2387 data with $I > 3\sigma(I)$ and 301 variables. For **2** (two independent molecules in the unit cell): $C_{46}H_{46}Ir_2O_2$, $M = 1015.32$, orthorhombic, space group $Pcab$ (no. 61), $a = 16.476(5)$, $b = 31.468(8)$, $c = 14.645(4)$ Å, $U = 7593(3)$ Å^3, $Z = 8$, $D_c = 1.78$ g cm^{-3}, μ(Mo-Kα) = 70.131 cm^{-1}, 9831 measured reflections, 7404 independent, $R = 0.0580$ ($R_w = 0.0638$) for 4071 data with $I > 3\sigma(I)$ and 451 variables. CCDC 182/761.

¶ ^{1}H NMR for **2** (CD_2Cl_2, 22 °C): δ 7.47 (d of d, J_1 7.26, J_2 1.32 Hz, 2 H, $C_{12}H_8$), 7.46 (d of d, J_1 7.26, J_2 1.32 Hz, 2 H, $C_{12}H_8$), 7.06 (d of t, J_1 7.26, J_2 1.32 Hz, 2 H, $C_{12}H_8$), 6.90 (d of t, J_1 7.26, 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. Calc. for $C_{23}H_{23}IrO$: C, 54.42; H, 4.57. Found. C, 54.24, H, 4.49%.

1 W. Schlenk and T. Weichel, *Ber.*, 1911, **44**, 1182; H. Schlubach, *Ber.*, 1915, **48**, 12; C. B. Wooster, *J. Am. Chem. Soc.*, 1928, **50**, 1388; W. E. Bachmann, *J. Am. Chem. Soc.*, 1933, **55**, 1179; P. J. Hamrick, Jr. and C. R. Hauser, *J. Am. Chem. Soc.*, 1959, **81**, 493; S. Selman and J. F. Easthan, *J. Org. Chem.*, 1965, **30**, 3804; E. L. Anderson and J. E. Casey, Jr., *J. Org. Chem.*, 1965, **30**, 3959; W. S. Murphy and D. J. Buckley, *Tetrahedron Lett.*, 1969, 2975; J. W. Huffman, in *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming, Pergamon, New York, 1991, vol. 8, ch. 1.4; G. M. Robertson, in *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming, Pergamon, New York, 1991, vol. 3, ch. 2.6.

2 J. E. McMurry and L. R. Krepiski, *J. Org. Chem.*, 1976, **41**, 3929; J. E. McMurry, M. P. Fleming, K. L. Kees and L. R. Krepiski, *J. Org. Chem.*, 1978, **43**, 3255; J. M. Pons and M. Santelli, *Tetrahedron Lett.*, 1982, **23**, 4937; J. E. McMurry, *Acc. Chem. Res.*, 1983, **16**, 405; 1974, **7**, 281; *Chem. Rev.*, 1989, **89**, 1513; A. Fürstner and B. Bogdanovic, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2442.

3 Z. Hou, K. Takamine, Y. Fujiwara and H. Taniguchi, *Chem. Lett.*, 1987, 2061; Z. Hou, K. Takamine, O. Aoki, H. Shiraishi, Y. Fujiwara and H. Taniguchi, *J. Chem. Soc., Chem. Commun.*, 1988, 668; *J. Org. Chem.*, 1988, **53**, 6077; H. Olivier, Y. Chauvin and L. Saussine, *Tetrahedron*, 1989, **45**, 165; Z. Hou, T. Yoshimura and Y. Wakatsuki, *J. Am. Chem. Soc.*, 1994, **116**, 11169; T. Yoshimura, Z. Hou and Y. Wakatsuki, *Organometallics*, 1995, **14**, 5382.

4 B. Bogdanovic, C. Kruger and B. Wermeckes, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 817.

5 Z. Hou, H. Yamazaki, K. Kobayashi, Y. Fujiwara and H. Taniguchi, *J. Chem. Soc., Chem. Commun.*, 1992, 722; Z. Hou, H. Yamazaki, Y. Fujiwara and H. Taniguchi, *Organometallics*, 1992, **11**, 2711.

6 J. E. Davies, J. Kopf and E. Weiss, *Acta Crystallogr., Sect. B*, 1982, **38**, 2251.

7 S. Brooker, F. T. Edelmann, T. Kottke, H. W. Roesky, G. M. Scheldrick, D. Stalke and K. H. Whitmire, *J. Chem. Soc., Chem. Commun.*, 1991, 144.

8 Z. Hou, A. Fujita, H. Yamazaki and Y. Wakatsuki, *J. Am. Chem. Soc.*, 1996, **118**, 2503.

9 S. Corbelin, J. Kopf and E. Weiss, *Chem. Ber.*, 1991, **124**, 2417.

10 Q. Shen, M. Qi and Y. Lin, *J.Organomet. Chem.*, 1990, **399**, 247.

11 H. R. Luss and D. L. Smith, *Acta Crystallogr., Sect. B*, 1972, **28**, 884.

12 Z. Hou, T. Miyano, H. Yamazaki and Y. Wakatsuki, *J. Am. Chem. Soc.*, 1995, **117**, 4421; Z. Hou, A. Fujita, H. Yamazaki and Y. Wakatsuki, *J. Am. Chem. Soc.*, 1996, **118**, 7843.

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