Supplementary Material (ESI) for Chemical Communications
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Supporting information

After 118 Years, the Isolation of Two Common Radical Anion Reductants as Simple, Stable Solids

Thomas A. Scott,[a] Betty A. Ooro,[a] David J. Collins,[a] Michael Shatruk,[b] Andrey Yakovenko,[c] Kim R. Dunbar,[c] and Hong-Cai Zhou*[a,c]

Experimental Procedure:

THF and diethyl ether were distilled with Na/K/benzophenone ketyl under N_2 before use; both solvents were degassed with N_2 prior to use. All other chemicals were purchased from standard commercial sources and used without further purification. All operations were conducted under a pure N_2 atmosphere using an inert atmosphere box or standard Schlenk techniques.

Preparation of $K_2(C_{10}H_8)_2(C_4H_8O)$:

0.500 g of naphthalene was dissolved in 17 mL of diethyl ether and placed in a small glass vial. A slight excess (1.1 eq) of K metal was added, followed by 3 mL of THF, deposited via pipet to the bottom of the flask under the ether. A green color quickly formed in the THF layer and the vial was sealed. Crystals formed in 2-3 days. These crystals were collected, washed with ether and dried *in vacuo*. Yield: 520 mg (~65%), m.p. not observed below 400 °C. Anal. Calc. C: 70.88%, H: 5.95; Found C: 70.07%, H: 6.28%.

Preparation of $K(Ph_2CO)$:

0.450 g of Ph_2CO was dissolved in 19 mL of diethyl ether and 1 mL of THF, and placed in a small glass vial. To this a slight excess (1.1 eq) of K metal was added, forming a blue solution; the vial was then sealed. Crystals formed within one week. These crystals were washed with ether and dried *in vacuo*. Yield: 255 mg (~47%), m.p. 214 °C. Anal. Calc. C: 70.55%; H: 4.55%. Found C: 69.88%; H: 4.73%.

Structure Determination

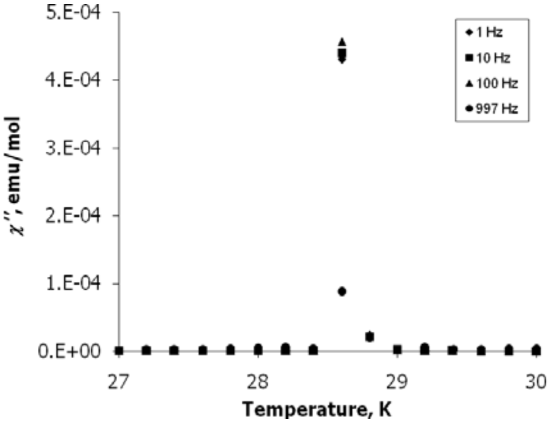
Single-crystal X-ray diffraction was performed on a Bruker Apex D8 CCD diffractometer

[a] *Department of Chemistry and Biochemistry, Miami University, Oxford,OH 45056, USA Country. Fax: +01 513 5290452; Tel: +01 513 5298091; E-mail: zhouh@muohio.edu*
[b] *Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306, USA*
[c] *Department of Chemistry, Texas A&M University, College Station, TX 77842, USA*

equipped with a fine-focus sealed-tube X-ray source (Mo-K$_\alpha$ radiation, λ = 0.71073 Å, graphite-monochromated). Crystals were mounted on glass fibers and maintained under a stream of N_2 at 213 K. Frames were collected with 0.3° intervals in φ and ω for 30 s/frame such that a hemisphere of data was collected. Raw data collection and cell refinement were done using SMART; data reduction was performed using SAINT+ and corrected for Lorentz and polarization effects. Absorption corrections were applied using the SADABS routine.[1] Structures were solved by direct method and refined by full-matrix least-squares on F^2 using SHELX-97.[2] Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to 1.2 × U_{eq} of the attached atom (1.5 × U_{eq} for methyl hydrogen atoms). If necessary, high-angle data were cut during the final least-squares refinement cycles. CCDC 689226 and 689227 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Magnetic Measurements

Magnetic susceptibility and magnetization measurements were carried out with a Quantum Design SQUID magnetometer MPMS-XL. DC magnetic measurements were performed in an applied field of 1000 Oe in a temperature range of 2-300 K. AC magnetic susceptibility measurements were performed in a 3 Oe AC field in an operating frequency range of 1-1000 Hz. The data were corrected for diamagnetic contributions calculated from the Pascal constants.



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[a] Department of Chemistry and Biochemistry, Miami University, Oxford,OH 45056, USA Country. Fax: +01 513 5290452; Tel: +01 513 5298091; E-mail: zhouh@muohio.edu
[b] Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306, USA
[c] Department of Chemistry, Texas A&M University, College Station, TX 77842, USA

Fig. S1 Temperature dependence of the imaginary part (χ'') of AC magnetic susceptibility of $K_2(C_{10}H_8)_2(C_4H_8O)$ at different frequencies of the applied AC magnetic field.

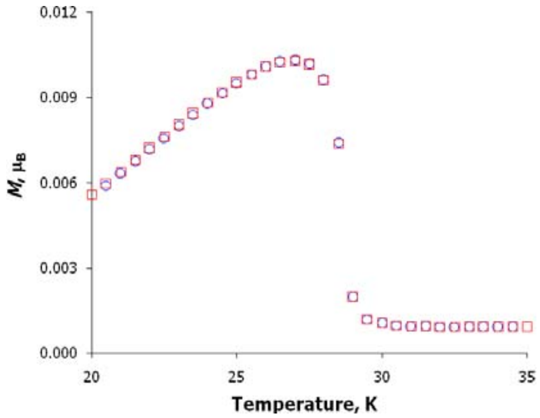

Fig. S2 Temperature dependence of zero-field-cooled (ZFC, blue circles) and field-cooled (FC, red squares) magnetization (M) of $K_2(C_{10}H_8)_2(C_4H_8O)$ measured in the applied DC magnetic field of 1000 G.

Electrochemical Measurements

Electrochemical measurements were made in CH_3CN with a CH Instruments Model 610A Electrochemical Analyzer using a Pt disk working electrode, Pt wire counter electrode, and a Ag wire reference electrode, with a 100 mV/s scan rate. All potentials are reported vs. Fc/Fc^+.

$K(C_{10}H_8)$ exhibits the $C_{10}H_8/[C_{10}H_8]^-$ redox couple at $E_{\frac{1}{2}} = -2.65$ V vs. Fc/Fc^+ (ferrocene/ferrocenium) in THF with the reduction wave at -3.00 V. $K(Ph_2CO)$ exhibits two redox pairs; one is a reversible pair corresponding to the $Ph_2CO/[Ph_2CO]^-$ couple at $E_{\frac{1}{2}}= -2.18$ V vs. Fc/Fc^+ in THF and the second is an irreversible pair corresponding to the $[Ph_2CO]^-/[Ph_2CO]^{2-}$ couple at $E_{\frac{1}{2}}= -3.01$ V. The first reduction wave is at -2.38 V, and the second at -3.28 V vs. Fc/Fc^+ in THF. Cyclic voltammograms are shown in Figure S3 and S4.

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[a] *Department of Chemistry and Biochemistry, Miami University, Oxford,OH 45056, USA Country. Fax: +01 513 5290452; Tel: +01 513 5298091; E-mail: zhouh@muohio.edu*
[b] *Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306, USA*
[c] *Department of Chemistry, Texas A&M University, College Station, TX 77842, USA*

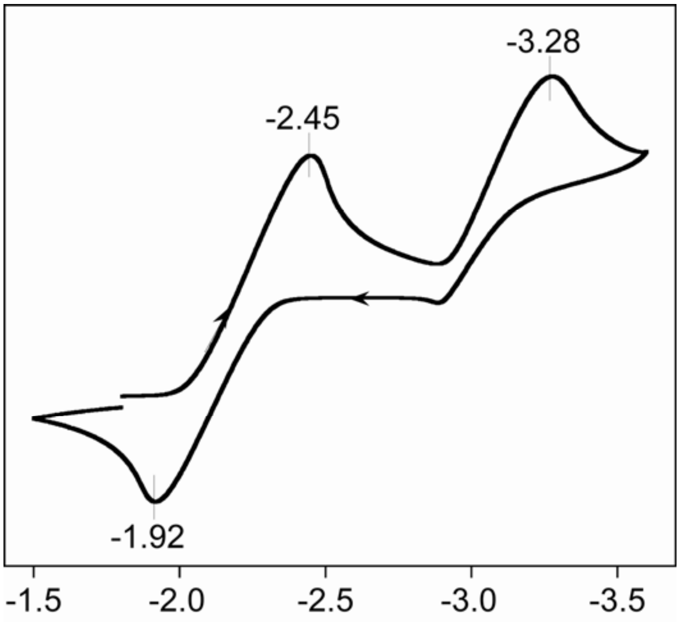

Fig. S3 Cyclic voltammogram K(Ph_2CO) in THF.

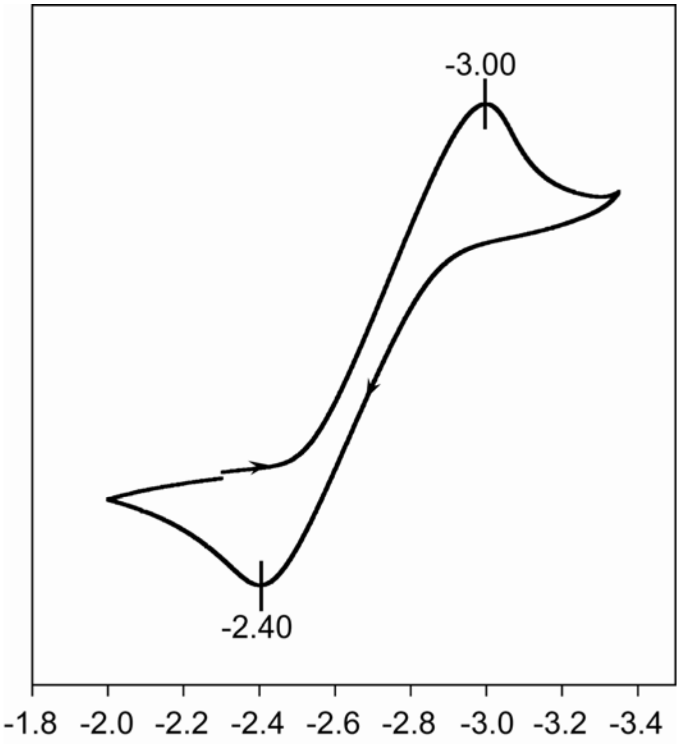

Fig. S4 Cyclic voltammogram of K($C_{10}H_8$) in THF.

[a] *Department of Chemistry and Biochemistry, Miami University, Oxford,OH 45056, USA Country. Fax: +01 513 5290452; Tel: +01 513 5298091; E-mail: zhouh@muohio.edu*
[b] *Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306, USA*
[c] *Department of Chemistry, Texas A&M University, College Station, TX 77842, USA*

Other Physical Measurements

Absorption spectra in the UV-visible range were recorded with an Agilent 8453 Spectrophotometer. Elemental analyses were performed by Canadian Microanalytical Service, Ltd. (Delta, BC, Canada).

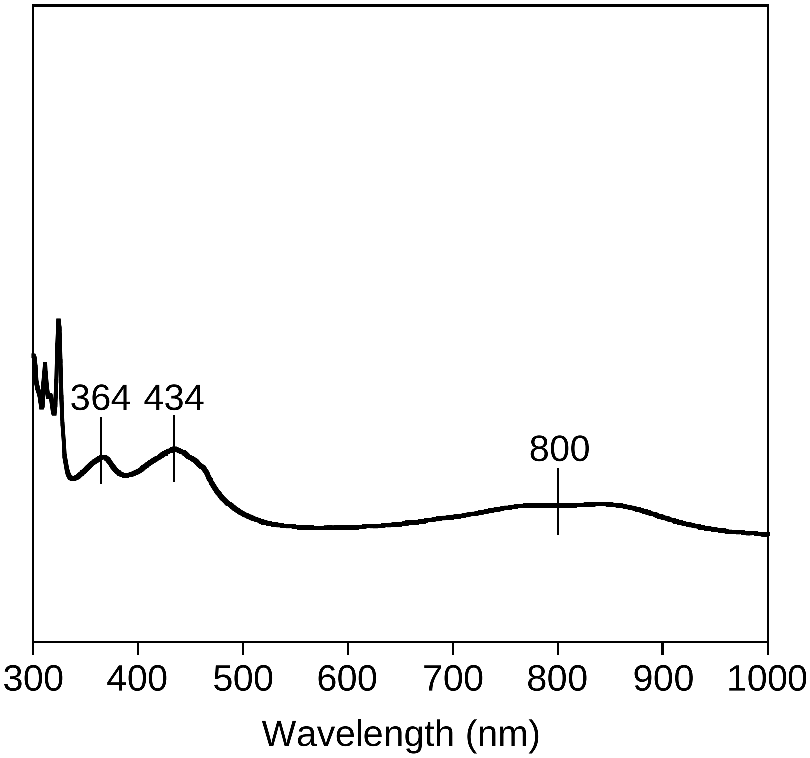

Fig. S5. The UV-vis spectrum of $K(C_{10}H_8)$ in THF/Et_2O.

[a] *Department of Chemistry and Biochemistry, Miami University, Oxford,OH 45056, USA Country. Fax: +01 513 5290452; Tel: +01 513 5298091; E-mail: zhouh@muohio.edu*
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[c] *Department of Chemistry, Texas A&M University, College Station, TX 77842, USA*

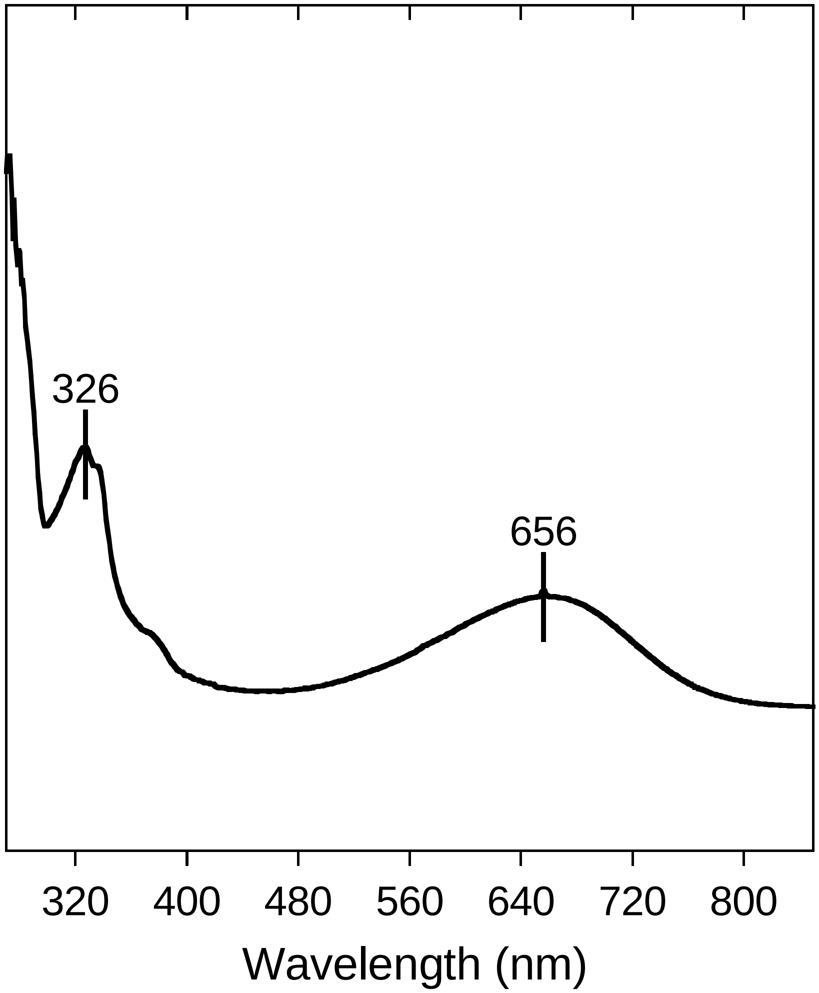

Fig. S6. The UV-vis spectrum of K(Ph_2CO) in THF.

(1) Bruker (2005). SADABS (Version 2.10), SAINT (Version 7.1) and APEX2 (Version RC13). Bruker AXS Inc., Madison, Wisconsin, USA.

(2) Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

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[a] Department of Chemistry and Biochemistry, Miami University, Oxford,OH 45056, USA Country. Fax: +01 513 5290452; Tel: +01 513 5298091; E-mail: zhouh@muohio.edu
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