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Electronic Supplementary Information

Evidence for a reactive (alkene)peroxoiridium(III) intermediate in the oxidation of an alkene complex with O_2

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Experimental Procedures

Materials. All reagents and solvents were purchased from commercial sources and were used as received, unless noted otherwise. Diethyl ether and toluene were deoxygenated by sparging with N_2 and purified by passage through two packed columns of molecular sieves under an N_2 pressure (MBraun solvent purification system). *n*-Pentane was dried over Na and distilled under N_2 prior to use.[1] Preparation and handling of air- and moisture-sensitive materials were carried out under an inert gas atmosphere by using either standard Schlenk and vacuum line techniques or a glovebox. Dioxygen was dried by passage through a short column of Drierite. Isotope-enriched $^{18}O_2$ (97% ^{18}O) was purchased from Cambridge Isotope Laboratories, Andover, MA, USA. [Ir{PhNC(NMe_2)NPh}(cod)] (**1**) was synthesized as previously described (cod = 1,5-cyclooctadiene).[2]

Physical Methods. NMR spectra were recorded on a Bruker Avance MicroBay 300, Avance 400 or Avance 500 spectrometer at ambient temperature, unless noted otherwise. ^1H, ^{13}C and ^{31}P chemical shifts are reported in parts per million (ppm) and were referenced to residual solvent peaks (for ^1H and ^{13}C NMR spectra) or an external standard [H_3PO_4 (85%, 0 ppm) for ^{31}P NMR spectra]. Two-dimensional correlated spectroscopy (COSY) and heteronuclear single-quantum coherence (HSQC) experiments were carried out on a Bruker Avance 500 spectrometer at 25 °C using the gradient versions of the COSY and HSQC pulse sequences, and the data were processed using the TopSpin 2.1 software package. For $^1H,^1H$ COSY, typical measurement parameters were as follows: time domain data points (TD), 2048 for TD and 512 for TD1; number of scans (NS), 8; and number of dummy scans (DS), 32. The data were processed with zero-filling to 4096 (TD) and 512 (TD1). For $^1H,^{13}C$ HSQC, typical measurement parameters were as follows: 2048 for TD and 200 for TD1; NS, 16; and DS, 16. The data were processed with zero-filling to 2048 (TD) and 1024 (TD1). The total measurement time for each experiment was approximately 2 h. Self-diffusion coefficients (*D*) were determined from stimulated-echo experiments using bipolar gradients acquired in two-dimensional mode (stebpgp1s). These experiments were performed on a Bruker Avance 400 spectrometer at 25 °C. Prior to each experiment, the diffusion time (delay between the midpoints of the gradients, Δ) and gradient length (δ) were optimized using the one-dimensional version of the pulse sequence (stebpgp1s1d). The data acquisition for each diffusion experiment took approximately 30 min. Data processing and analysis to determine *D* were carried out within the TopSpin 2.1 software package.

IR spectra were recorded on a Bruker Vertex 70 Fourier-transform IR spectrometer using samples prepared by grinding the solid compound with KBr and pressing the mixture into a disk. Low-resolution mass spectral data were acquired on a quadrupole ion trap ThermoFinnigan LCQ Deca mass spectrometer using an electrospray ionization source or on a single quadrupole ThermoFinnigan Voyager mass spectrometer using an electron impact ionization source (equipped with a solids probe). High-resolution mass spectral data were acquired on a time-of-flight Waters GCT Premier mass spectrometer using an electron impact ionization source (equipped with a solids probe). UV–Visible spectra were recorded on an HP 8453A diode array spectrophotometer (Agilent Technologies).

Generation and Characterization of [Ir{PhNC(NMe_2)NPh}(η^4-cod)(η^2-O_2)] (2). In a typical experiment, a 15–20 mM solution of **1** (4.0–5.4 mg, 0.0075–0.010 mmol) in 0.5 ml of

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C_6D_6 was placed in an NMR tube and purged with $O_2(g)$ at 20 °C for 40 s. The progress of the reaction was monitored by ^{1}H NMR spectroscopy. Under these conditions, **1** (bright yellow solution) converted into the intermediate, **2** (pale yellow solution), in about 3 h, and **2** was typically fully decayed (dark green solution) within 12 h after the addition of O_2 to **1**. For quantification, 5 equiv of 1,2-dichloroethane (3.0–3.9 μl, 3.8–4.9 mg, 0.038–0.050 mmol) was added to the solution of **2**, and the yield was estimated by comparing the integrations of the 1,2-dichloroethane (δ, 2.90 ppm) and alkene proton signals (ca. 75%). For IR spectroscopy, 0.15 ml of a solution of **2** was mixed with KBr. The mixture was evaporated to dryness (20 °C, *in vacuo*) and pressed into a disk. For labeling experiments, 5 ml (ca. 0.2 mmol) of $^{18}O_2$ (97% ^{18}O) was added to a 15–20 mM solution of **1** (0.0075–0.010 mmol) in 0.5 ml of C_6D_6.

^{1}H NMR (500 MHz, C_6D_6, δ): 7.35 (br d, 2H, Ar H), 7.30 (d, J = 8.1 Hz, 2H, Ar H), 7.15 (Ar H; this signal partially overlaps with the residual solvent peak), 7.09 (t, J = 7.7 Hz, 2H, Ar H), 6.96 (t, J = 7.2 Hz, 1H, Ar H), 6.88 (t, J = 7.7 Hz, 1H, Ar H), 4.74 (br dt, 1H, =C*H*CH$_2$–), 4.55 (br dt, 1H, =C*H*CH$_2$–), 4.14 (br dt, 1H, =C*H*CH$_2$–), 4.01 (br dt, 1H, =C*H*CH$_2$–), 2.34–2.19 (m, 3H, =CHC*H*$_2$–), 2.17–2.09 (m, 1H, =CHC*H*$_2$–), 2.06–1.98 (m, 1H, =CHC*H*$_2$–), 2.03 (s, 6H, NCH$_3$), 1.94–1.88 (m, 1H, =CHC*H*$_2$–), 1.70–1.60 (m, 2H, =CHC*H*$_2$–). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.35 (br d, 4H, Ar H), 7.23–7.15 (m, 3H, Ar H), 7.11–7.08 (m, 2H, Ar H), 6.97 (t, J = 7.1 Hz, 1H, Ar H), 4.63–4.56 (m, 1H, =C*H*CH$_2$–), 4.53–4.46 (m, 1H, =C*H*CH$_2$–), 4.14–4.05 (m, 1H, =C*H*CH$_2$–), 3.93–3.84 (m, 1H, =C*H*CH$_2$–), 2.69–2.59 (m, 2H, =CHC*H*$_2$–), 2.56 (s, 6H, NCH$_3$), 2.54–2.27 (m, 4H, =CHC*H*$_2$–), 2.18–2.05 (m, 2H, =CHC*H*$_2$–). IR (KBr, cm^{-1}): 865 (ν_{OO}), 575 and 459 (ν_{IrO}). IR of **2**-$^{18}O_2$ (KBr, cm^{-1}): 813 (ν_{OO}), 550 (sh) and 442 (ν_{IrO}).

For comparison, ^{1}H NMR of **1** (300 MHz, C_6D_6, δ): 7.12 (t, J = 7.4 Hz, 4H, Ar H), 6.83 (t, J = 7.4 Hz, 2H, Ar H), 6.77 (d, J = 7.3 Hz, 4H, Ar H), 3.90 (br m, 4H, =C*H*CH$_2$–), 2.14 (br m, 4H, =CHC*H*$_2$–), 1.99 (s, 6H, NCH$_3$), 1.42 (m, 4H, =CHC*H*$_2$–).

Reaction of 2 with Triphenylphosphine. A solution of **2** in C_6D_6 was prepared as described above (ca. 3 h for the formation of **2**) and then purged with Ar for 5 min to remove excess O_2. A solution of 0.075–0.100 mmol of PPh_3 (10 equiv with respect to Ir) in 0.2 ml of C_6D_6 was added to the solution of **2**, and the progress of the reaction was monitored by ^{31}P NMR spectroscopy. The intermediate was fully decayed within 4 h (pale orange solution). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6, δ): 25.5 (s, $OPPh_3$), –4.4 (s, PPh_3), –9.1 (s).

Reaction of the Decay Products of 2 with 1,5-Cyclooctadiene. A 15–20 mM solution of **1** in C_6D_6 was purged with O_2 as described above, allowed to stand for at least 16 h, and then purged with Ar for 5 min to remove excess O_2. After addition of 0.015–0.020 or 0.075–0.100 mmol of cod (2 or 10 equiv with respect to Ir), the solution was kept at 20 °C for 1 d and then heated at 70 °C for 1 d (NMR tube equipped with a J. Young valve). During this time the color of the solution changed from dark green to orange. 4-cycloocten-1-one[3] and **1** were identified as products by ^{1}H NMR spectroscopy and EIMS. Quantifications (against 1,2-dichloroethane as a standard) were performed in triplicate. The average yields were 0.88 (±0.13) equiv of 4-cycloocten-1-one and 0.30 (±0.05) equiv of **1**. Data for 4-cycloocten-1-one were as follows: ^{1}H NMR (300 MHz, C_6D_6, δ): 5.65 (m, 1H, =C*H*CH$_2$–), 5.37 (m, 1H, =C*H*CH$_2$–), 2.66 (m, 1H, =CHC*H*$_2$–), 2.24 (m, 3H, =CHC*H*$_2$–), 2.10 (m, 2H, =CHC*H*$_2$–), 1.40–1.31 (m, 4H, =CHC*H*$_2$–). EIMS (70 eV) m/z: $M^{+\bullet}$ calcd for $C_8H_{12}O$, 124.1; found, 124.3 (the expected fragmentation pattern[4] was observed as follows: 109.3, 96.3, 81.3, 67.2, 54.2). For the reaction carried out using $^{18}O_2$, EIMS (70 eV) m/z: 126.3 ($M^{+\bullet}$; fragmentation pattern: 111.3, 96.3, 81.3, 67.2, 54.2).

References

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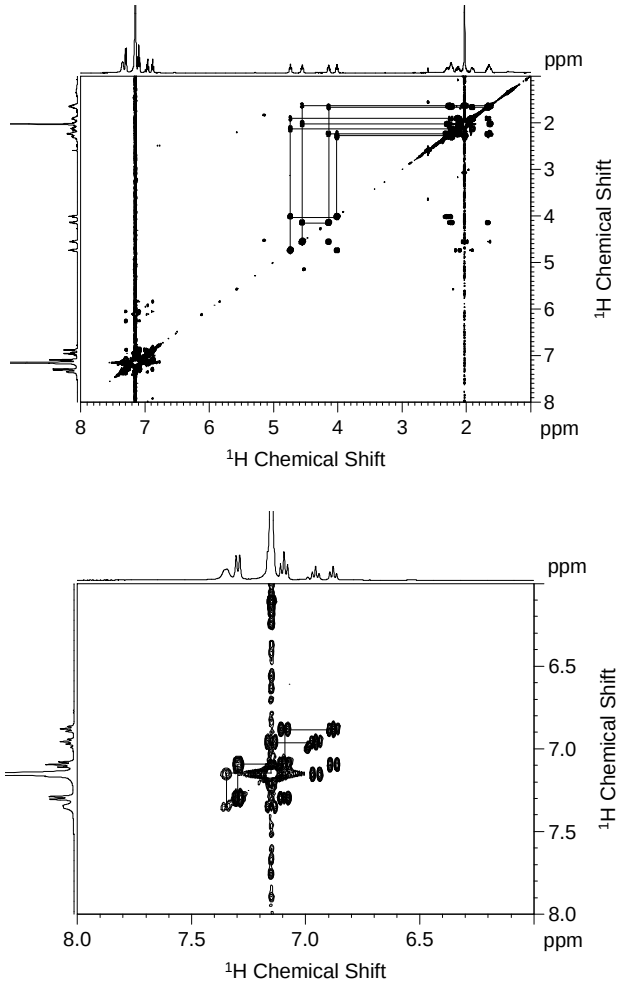

Figure S1. Top: ^{1}H,^{1}H COSY spectrum of **2** in benzene-d_6 (ca. 15 mM, 500 MHz, 25 °C). The solid lines indicate correlations among alkene proton resonances and between alkene and methylene proton resonances. Bottom: Expanded view of the aromatic region of the ^{1}H,^{1}H COSY spectrum of **2**. The solid lines indicate correlations among aromatic proton resonances.

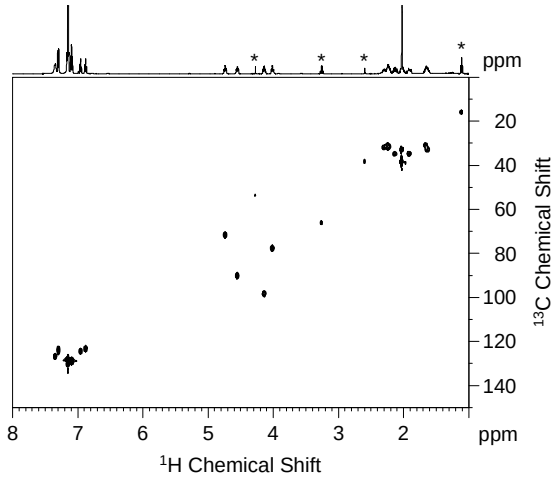

Figure S2. ^{1}H,^{13}C HSQC spectrum of **2** in benzene-d_6 (ca. 15 mM, 500 MHz, 25 °C). The asterisks denote solvent peaks (CH_2Cl_2, Et_2O, and an unknown contaminant).

Table S1. ^{1}H and ^{13}C chemical shifts, δ (ppm), from the ^{1}H,^{13}C heteronuclear single-quantum coherence (HSQC) spectrum of [Ir{PhNC(NMe$_2$)NPh}(cod)(O$_2$)] (**2**) in benzene-d_6.

Assignment		δ(^{1}H)	δ(^{13}C)
Ar	Group A	7.35	126.8
		7.15[a]	128.0[a]
		6.96	124.4
	Group B	7.30	123.9
		7.09	128.9
		6.88	123.3
=*CH*CH$_2$–	1-H, C-1	4.74	71.7
	2-H, C-2	4.01	77.7
	5-H, C-5	4.55	90.1
	6-H, C-6	4.14	98.3
=CH*CH$_2$*–	3-H$_{ab}$, C-3	2.31, 2.23	32.0
	4-H$_{ab}$, C-4	2.02, 1.63	32.8
	7-H$_{ab}$, C-7	2.23, 1.66	31.4
	8-H$_{ab}$, C-8	2.13, 1.91	34.8
NCH$_3$		2.03	38.1

[a] The resonance signals centered at δ(^{1}H) = 7.15 ppm and δ(^{13}C) = 128.0 ppm partially overlap with the residual solvent peaks.

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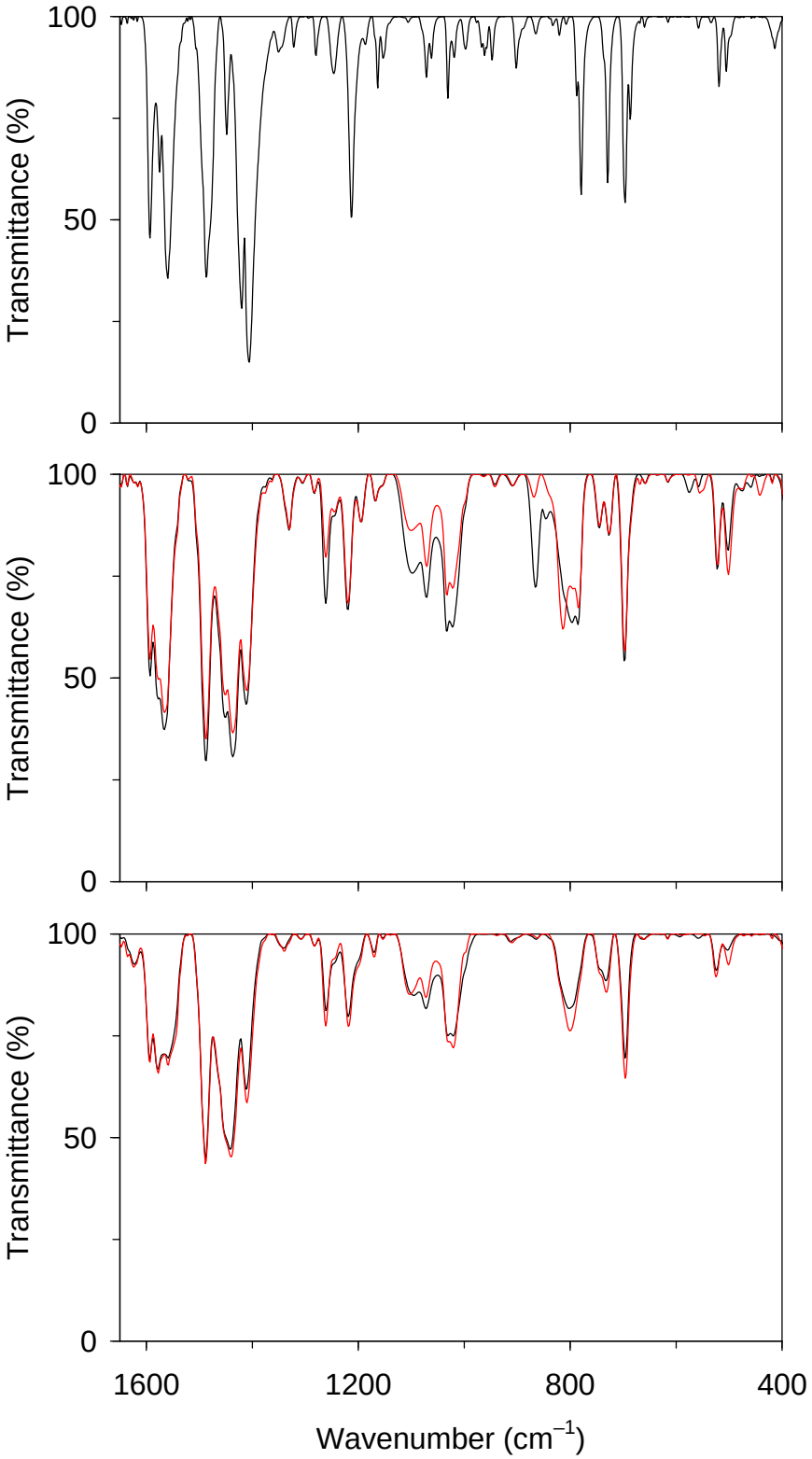

Figure S3. Top: IR spectrum of **1** (—, black). Middle: IR spectra of **2** (—, black) and **2**-$^{18}O_2$ (—, red). Bottom: IR spectra of the decay products of **2** (—, black) and **2**-$^{18}O_2$ (—, red).

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Determination of the Self-Diffusion Coefficients of 1 and 2

Diffusion ^{1}H NMR experiments to determine *D* values were conducted in triplicate, and, for each experiment, data of six (**1**) or ten (**2**) suitable peaks were averaged. The average *D* values from three measurements were 8.4 (±0.1) · 10^{-10} and 8.2 (±0.3) · 10^{-10} $m^2 \cdot s^{-1}$ for **1** and **2**, respectively. Intermediate **2** was found to decay by ≤10% over the course of each measurement, introducing a minor error into *D*. Shown below are representative results for the NMe_2 resonance signals of **1** and **2**. The plots in Figure S4 confirm the expected linear relationship between $\ln(I/I_0)$ and $G^{2.5}$

```
SIMFIT RESULTS for 1
==============

INTENSITY fit : Diffusion : Variable Gradient :
I=I[0]*exp(-D*SQR(2*PI*gamma*Gi*LD)*(BD-LD/3)*1e4)
16 points for Peak 5,  NMe2 resonance signal
Converged after 31 iterations!

Results     Comp. 1
I[0]           =  9.978e-001
Diff Con.      =  8.569e-010 m2/s
Gamma          =  4.258e+003 Hz/G
Little Delta   =      5.000m
Big Delta      =     26.950m

RSS   =   6.239e-005
SD    =   1.975e-003

Point     Gradient       Expt          Calc       Difference
    1   6.740e-001    1.000e+000    9.960e-001    -3.970e-003
    2   2.765e+000    9.691e-001    9.686e-001    -4.901e-004
    3   4.855e+000    9.107e-001    9.107e-001    -4.593e-005
    4   6.945e+000    8.262e-001    8.276e-001    1.404e-003
    5   9.036e+000    7.252e-001    7.271e-001    1.921e-003
    6   1.113e+001    6.158e-001    6.175e-001    1.712e-003
    7   1.322e+001    5.040e-001    5.069e-001    2.941e-003
    8   1.531e+001    4.006e-001    4.023e-001    1.717e-003
    9   1.740e+001    3.086e-001    3.087e-001    8.304e-005
   10   1.949e+001    2.308e-001    2.289e-001    -1.889e-003
   11   2.158e+001    1.663e-001    1.641e-001    -2.139e-003
   12   2.367e+001    1.159e-001    1.138e-001    -2.183e-003
   13   2.576e+001    7.857e-002    7.621e-002    -2.354e-003
   14   2.785e+001    5.113e-002    4.936e-002    -1.762e-003
   15   2.994e+001    3.254e-002    3.090e-002    -1.641e-003
   16   3.203e+001    2.010e-002    1.870e-002    -1.395e-003
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SIMFIT RESULTS for **2**
==========

INTENSITY fit : Diffusion : Variable Gradient :
I=I[0]*exp(-D*SQR(2*PI*gamma*Gi*LD)*(BD-LD/3)*1e4)
16 points for Peak 9, NMe2 resonance signal
Converged after 34 iterations!

Results	Comp. 1	
I[0]	=	9.960e-001
Diff Con.	=	8.577e-010 m2/s
Gamma	=	4.258e+003 Hz/G
Little Delta	=	5.000m
Big Delta	=	26.950m

RSS = 1.151e-004
SD = 2.682e-003

Point	Gradient	Expt	Calc	Difference
1	6.740e-001	1.000e+000	9.942e-001	-5.792e-003
2	2.765e+000	9.694e-001	9.669e-001	-2.516e-003
3	4.855e+000	9.074e-001	9.089e-001	1.526e-003
4	6.945e+000	8.232e-001	8.260e-001	2.794e-003
5	9.036e+000	7.220e-001	7.255e-001	3.568e-003
6	1.113e+001	6.119e-001	6.161e-001	4.200e-003
7	1.322e+001	5.039e-001	5.057e-001	1.837e-003
8	1.531e+001	4.014e-001	4.013e-001	-1.201e-004
9	1.740e+001	3.087e-001	3.078e-001	-8.452e-004
10	1.949e+001	2.295e-001	2.282e-001	-1.347e-003
11	2.158e+001	1.656e-001	1.636e-001	-2.039e-003
12	2.367e+001	1.156e-001	1.133e-001	-2.217e-003
13	2.576e+001	7.865e-002	7.590e-002	-2.750e-003
14	2.785e+001	5.168e-002	4.914e-002	-2.536e-003
15	2.994e+001	3.256e-002	3.075e-002	-1.810e-003
16	3.203e+001	2.018e-002	1.860e-002	-1.572e-003

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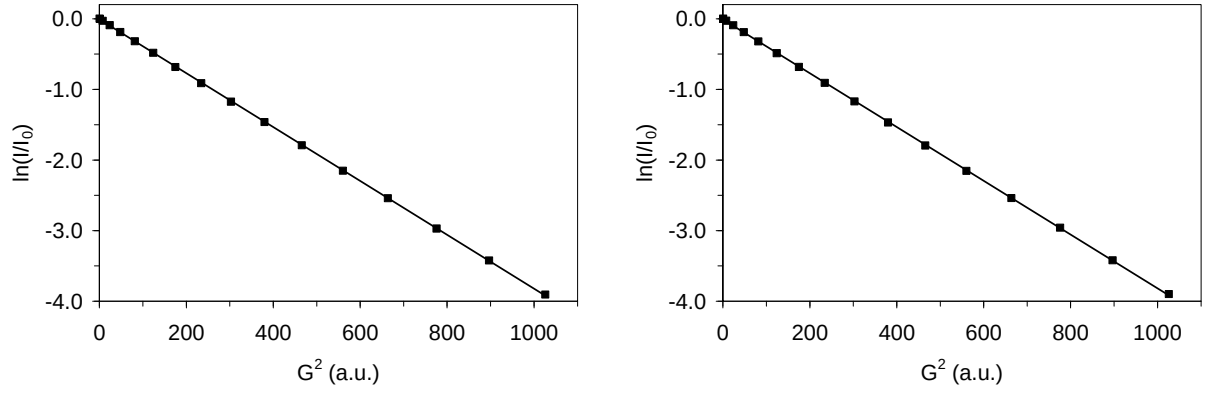

Figure S4. Plots of the natural logarithm of the intensity quotient, $\ln(I/I_0)$, *versus* the square of the gradient strength, G^2, for the NMe_2 resonance signals of **1** (left; $R^2 = 0.99996$) and **2** (right; $R^2 = 0.99995$).

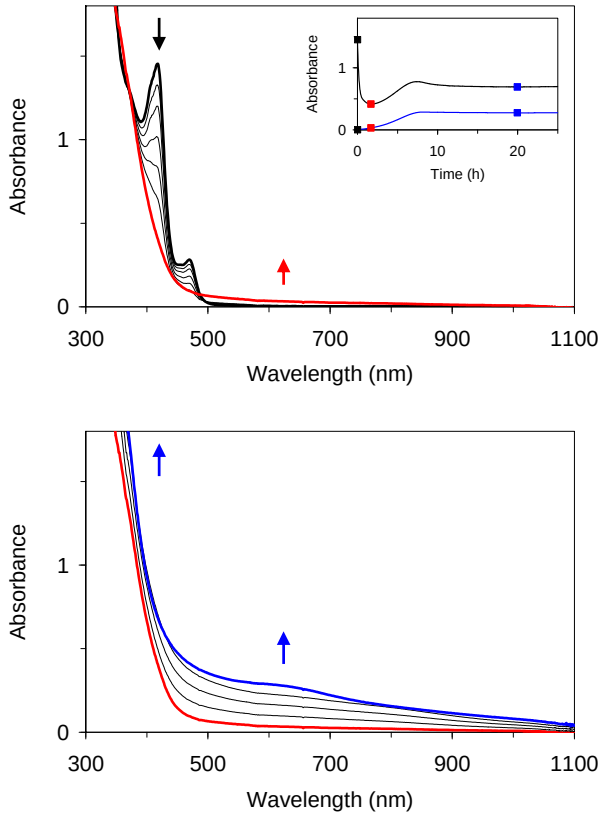

Figure S5. Reaction of 2 mM **1** in toluene with O_2 at 20 °C as monitored by electronic absorption spectroscopy (path length, 0.5 cm). Top: Decay of **1** (—, black) to afford intermediate **2** (—, red; t = 1.7 h). Bottom: Decay of **2** (—, red) to afford the product solution (—, blue; t = 20 h). Inset (top): Time course of the reaction of **1** with O_2 [λ = 417 nm (—, black) and 630 nm (—, blue)]. The squares indicate the reaction times associated with the spectra shown (black, **1**; red, **2**; and blue, decay products of **2**).

Table S2. Mass-to-charge ratios (m/z) from the electrospray ionization (ESI) and electron impact (EI) mass spectra of the decay products of [Ir{PhNC(NMe_2)NPh}(cod)(O_2)] (**2**).[a–c]

	ESI(+)MS				EIMS	
Complex	$\{LH + H\}^+$	$\{\mathbf{2} - O_2H\}^+$	$\{\mathbf{2} - OH\}^+$	$\{\mathbf{2} - H\}^+$	$\{\mathbf{2} - H_2O\}^{+\bullet}$	$\{IrL_3\}^{+\bullet}$
Found	240.2	538.3	554.2	570.1	553.1712	907.3577
Calcd	240.2	538.2	554.2	570.2	553.1705	907.3662
Found ($^{18}O_2$)	240.2	538.4	556.3	574.3	555.4	907.5

[a] The reaction of [Ir{PhNC(NMe_2)NPh}(cod)] (**1**) with O_2 (or $^{18}O_2$) was carried out as described in the Experimental Procedures Section, and the resulting solution was allowed to stand for at least 16 h. [b] LH = PhN=C(NMe_2)NHPh. [c] High-resolution mass spectral data are reported with four decimal places.