

Supporting Information

Oxygen Binding to [Pd(L)(L')] (L = NHC, L' = NHC or PR₃, NHC = N-Heterocyclic Carbene). Synthesis and Structure of a Paramagnetic *trans*-[Pd(NHC)₂(η¹-O₂)₂] Complex

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A. Synthetic and Thermochemical Experiments

General Considerations. Unless stated otherwise all reactions were carried out inside an MBraun or Vacuum Atmospheres glovebox or utilizing Schlenk tube techniques under inert atmosphere conditions. Solvents were purified by distillation under argon from an appropriate drying agent into flame dried glassware. NMR spectra were recorded on either a Bruker 400 MHz or a Bruker 300 MHz NMR spectrometer. Calorimetric measurements were performed using a Setaram Calvet C-80 or modified Guild Solution Calorimeter as described previously.¹ Elemental analyses were performed at London Metropolitan University. Magnetic susceptibility measurements were made using a Johnson-Matthey MSB-Auto Magnetic Susceptibility Balance and diamagnetic corrections made according to the literature². Pd -NHC complexes and their O₂ derivatives were prepared by methods strictly analogous to those reported previously³. Representative procedures for preparation and reactions of new complexes are described below.

NMR Studies of Reaction of Pd(NHC)₂ (NHC = IPr, SIPr) and O₂ at Room Temperature.

A solution of 5 mg Pd(IPr)₂ was weighed into an NMR tube in the glove box and dissolved in 0.5 mL C₆D₆ fitted with a screw cap and Teflon-lined silicone rubber septum. An NMR spectrum was taken and then 3ml of pure O₂ gas was added to the tube and it was shaken. A second NMR spectrum recorded 16 minutes later showed complete disappearance of the signals due to the diamagnetic starting material and conversion to a paramagnetic product as shown in Figure S1a below. ¹H NMR (400MHz, C₆D₆): δ=7.16 (t, under peak of C₆D₆ at 7.16ppm, 4H), 6.65 (s, broad, 8H), 6.11 (s, broad, 4H), 3.29 (s, very broad, 32H), 1.67 (s, broad, 24H).

The spectrum of starting material Pd(IPr)₂ and product [Pd(IPr)₂(O₂)₂] are shown as an overlay in Figure S1b.

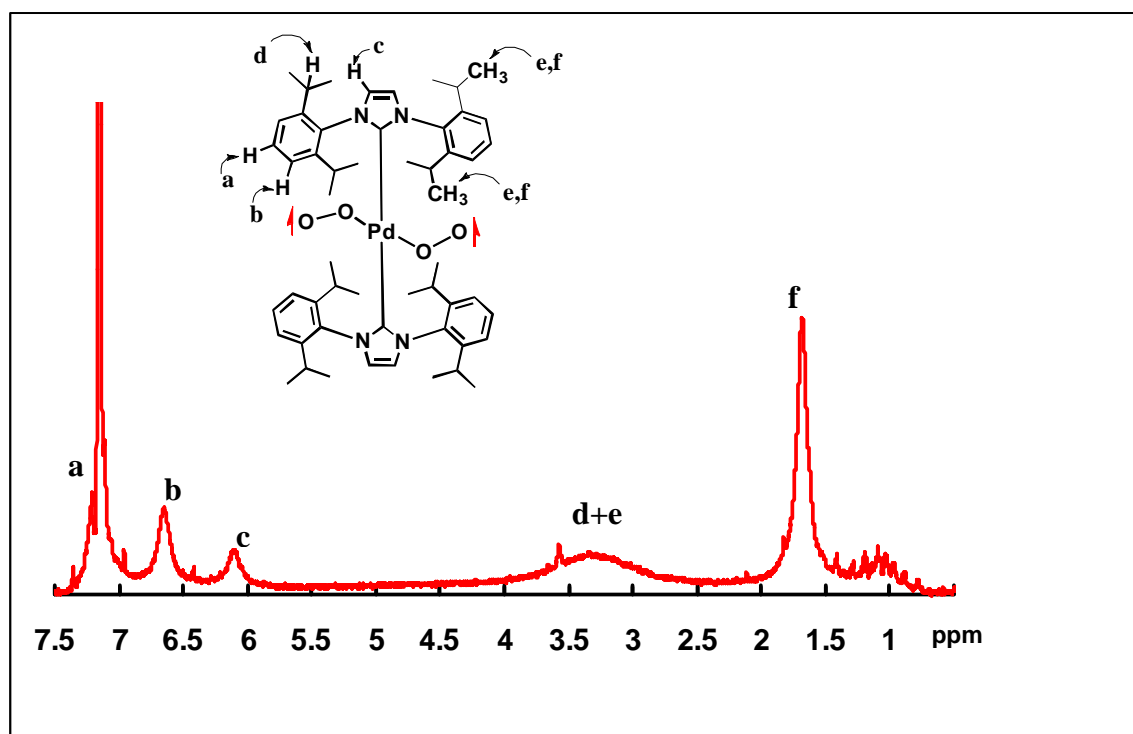


Figure S1a. ^1H NMR spectrum in C_6D_6 of $[\text{Pd}(\text{IPr})_2(\text{O}_2)_2]$

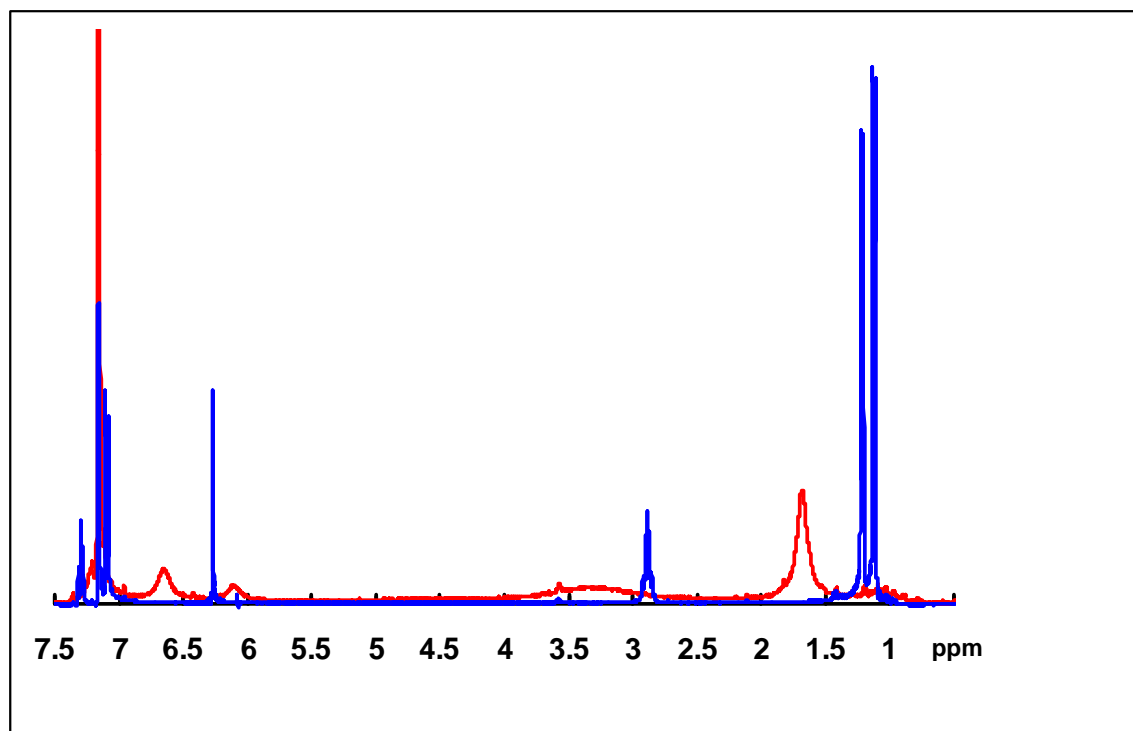


Figure S1b. ^1H NMR spectrum in C_6D_6 of $\text{Pd}(\text{IPr})_2$ before addition of O_2 (blue spectrum) and after addition of O_2 (red spectrum). The red spectrum has been multiplied by 4 due to its broad nature.

In a similar manner, a solution of $\text{Pd}(\text{SIPr})_2$ in C_6D_6 was prepared inside the glovebox and the Schlenk flask containing the solution was brought out of the glovebox. Pure O_2 was added to the flask. After shaking the flask for a few minutes, the color of the solution changed from orange-red to orange-yellow. Excess O_2 was evacuated out of the flask. The NMR spectrum of in C_6D_6 of $[\text{Pd}(\text{SIPr})_2(\text{O}_2)_2]$ is shown in Figure S1c. For both $[\text{Pd}(\text{IPr})_2(\text{O}_2)_2]$ and $[\text{Pd}(\text{SIPr})_2(\text{O}_2)_2]$ evacuation to dryness and redissolving in C_6D_6 did not result in regeneration of the starting $\text{Pd}(\text{NHC})_2$ complex.

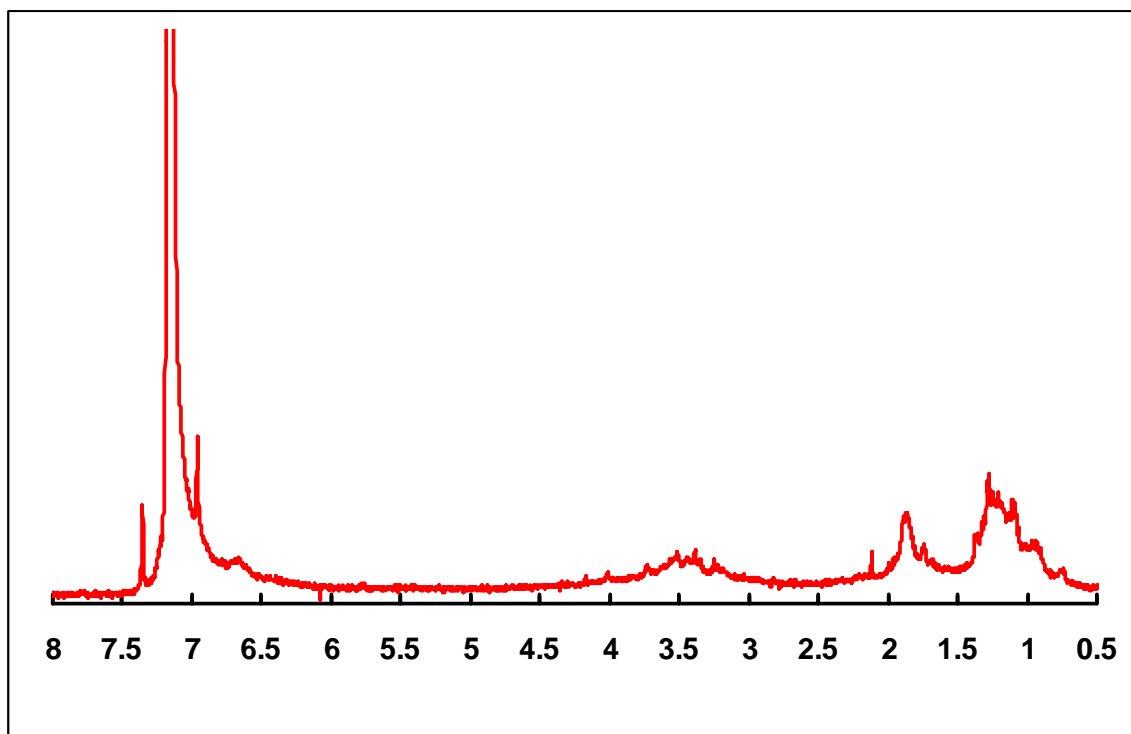


Figure S1c. ^1H NMR spectrum in C_6D_6 of $[\text{Pd}(\text{SIPr})_2(\text{O}_2)_2]$

UV-Visible Spectra before and after addition of O_2 to $\text{Pd}(\text{IPr})(\text{P}(\text{p-tolyl})_3)$ and $\text{Pd}(\text{IPr})_2$

In the glove box a 1.4 mm solution of $\text{Pd}(\text{IPr})(\text{P}(p\text{-tolyl})_3)$ in toluene was prepared. An aliquot of this solution was loaded into a UV-Vis cell. The cell was sealed, taken from the glove box, and a UV-Vis spectrum recorded prior to exposure to O_2 . The remainder of the solution was loaded in to a screw cap test tube fitted with a teflon septum. The test tube was taken from the glove box and purged with an atmosphere of pure O_2 . The color was immediately bleached. Spectral data are shown in Figure S2.

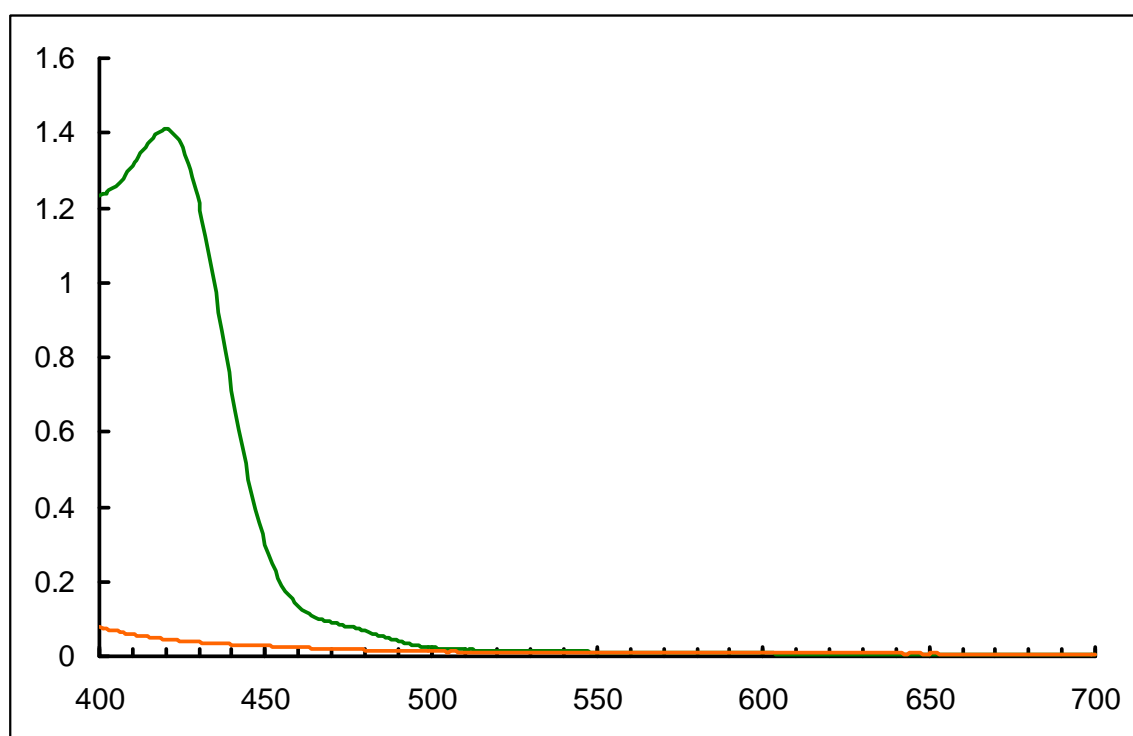


Figure S2. UV-Vis spectra of $\text{Pd}(\text{IPr})(\text{P}(p\text{-tolyl})_3)$ 1.4 mm in toluene) before (green spectrum) and after (orange spectrum) addition of O_2 .

In a similar manner to that described above, spectral data were recorded for $\text{Pd}(\text{IPr})_2$. This complex appears yellow in dilute solution, yellow-orange in more concentrated solution, and red-orange as a solid or in highly concentrated solution. Spectral data are shown in Figure 3, as well as a more concentrated spectrum.

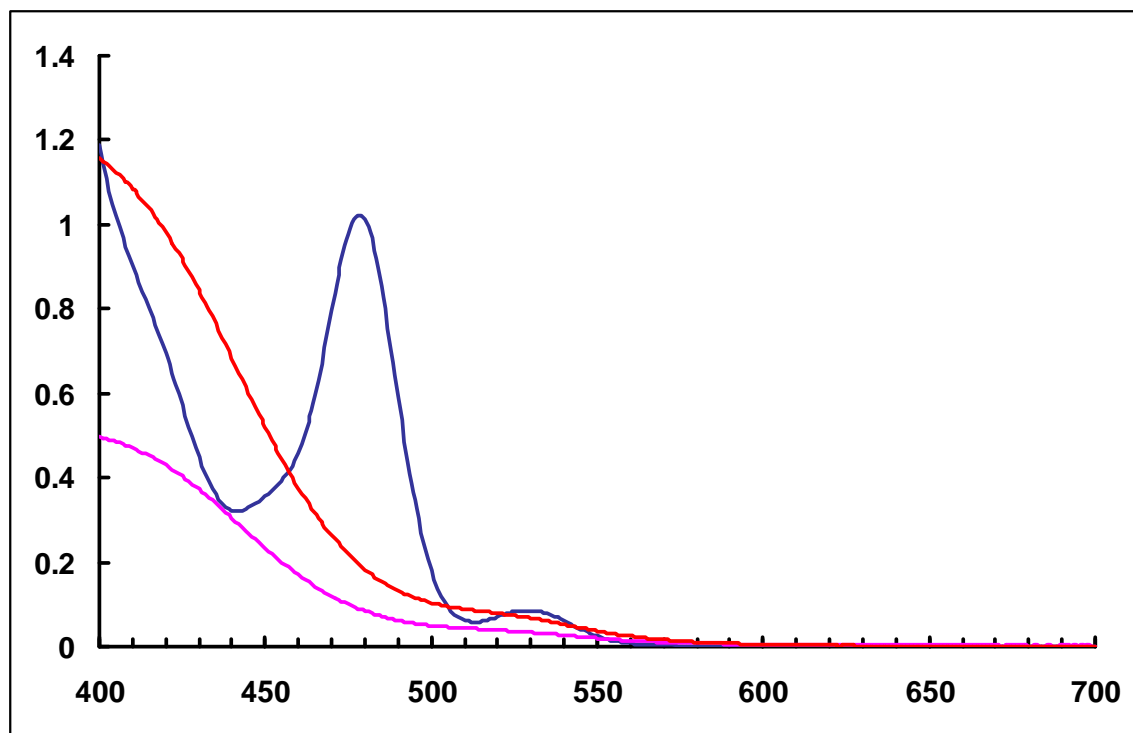


Figure S3. UV-Vis spectra of [Pd(IPr)₂] (1.1 mM in toluene) before (blue spectrum) and after (red spectrum) addition of O₂. The pink spectrum is of a more concentrated solution of [Pd(IPr)₂](O₂)₂.

Synthesis and Recrystallization of *trans*-[Pd(IPr)₂(O₂)₂].

In a Schlenk tube in the glovebox, 100 mg of Pd(IPr)₂ was dissolved in 3 mL of THF. It was exposed to one atmosphere of pure O₂ for 10 minutes and evaporated to dryness and dried *in vacuo* overnight. The complex so formed is spectroscopically and analytically pure in essentially quantitative yield. Elemental analysis was performed on this sample: Chemical Formula: C₅₄H₇₂N₄O₄Pd; Molecular Weight: 947.5; Theoretical: C, 68.44; H, 7.66; N, 5.91; Found: C, 68.58 ; H, 7.71 ; N, 5.82 .

Magnetic susceptibility measurements were performed on a sample that had been further recrystallized (in \approx 40 % yield) by filtering a saturated heptane solution into a Schlenk tube,

reducing the volume and storing overnight in the freezer at - 20 °C. Crystals suitable for X-ray crystallography were obtained by recrystallization from hexane.

Qualitative Study of Rate of Reaction of Pd(IPr)₂ and O₂ (1 atm) at -78 °C in Toluene Solution.

A stock solution of 49 mg recrystallized Pd(IPr)₂ was prepared in 5 mL toluene in the glovebox under an argon atmosphere and divided equally between two identical 20 mL Schlenk tubes. The tubes were taken from the glove box and were identical in their yellow-orange color. One of the tubes was exposed to 1 atm of O₂ and shaken for approximately 5 minutes. During this time the color of the solution changed to the red-orange color characteristic of [Pd(IPr)₂(O₂)₂]. Both tubes were then placed in a dry-ice/acetone bath at -78 °C and their colors again compared. At that time the atmosphere of the tube that had not been exposed to O₂ was evacuated and filled with pure O₂ gas. The solution was shaken but kept at -78 °C. During a period of 5-10 minutes there was no visible color change indicating a lack of reaction. The tube was then taken from the dry ice bath, and allowed to slowly warm to room temperature. During warm up at a temperature estimated to be T ≈ - 40 °C the color of the tube originally under Ar began to change color and by the time it had reached T ≈ 0 °C it matched in color the authentic sample of [Pd(IPr)₂(O₂)₂]. Identical experiments performed with Pd(P-p-tolyl)₃(IPr) and Pd(IMes)₂ showed that reaction with O₂ was rapid even at -78 °C and only for Pd(IPr)₂ did we observe a slow rate of reaction in a dry ice/acetone bath.

Synthesis of [Pd(IPr)₂(OOH)₂] and [Pd(SIPr)₂(OOH)₂].

In a test tube 0.053g Pd(IPr)₂ was dissolved in 4 mL of C₆D₆ inside the glovebox. Then the tube was brought out of the glovebox and pure O₂ was added to the solution. The color of the

solution changed from fluorescent orange to orange-red. After evacuating the excess O_2 , the tube was again taken into the glovebox and 0.0255g $HMo(CO)_3Cp$ solid was added to the solution. The solution immediately turned to the red-purple color characteristic of $[Mo(CO)_3Cp]_2$. The solution was filtered into an NMR tube and showed quantitative conversion of $HMo(CO)_3Cp$ to $[Mo(CO)_3Cp]_2$ with a chemical shift near 4.65 ppm as shown in Figure S4. A clear red solution was obtained. Peaks assigned to $[Pd(IPr)_2(OOH)_2]$: 1H NMR (400MHz, C_6D_6): $\delta=7.28$ (t, 4H), (d, under peak of C_6D_6 at 7.16ppm, 8H), 6.42 (s, 4H), 3.99 (s, 2H), 3.03 (sept, 8H), 1.17 (d, 24H), 1.00 (d, 24H) (Different chemical shifts of protons e and f depend on their relative position to the Pd metal center.)

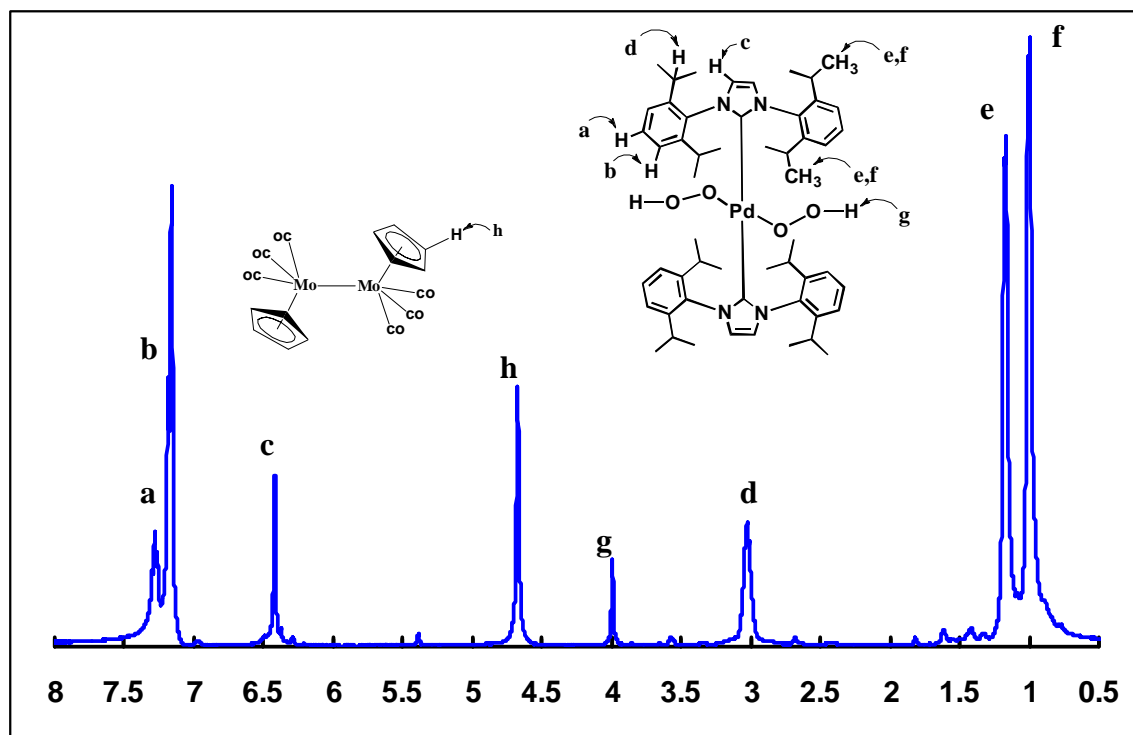


Figure S4. NMR spectrum of the reaction in C_6D_6 of $[Pd(IPr)_2(O_2)_2]$ and $HMo(CO)_3Cp$.

Attempts to grow X-Ray quality crystals of $[\text{Pd}(\text{IPr})_2(\text{OOH})_2]$ were not successful. Similar procedures were utilized to synthesize $[\text{Pd}(\text{SIPr})_2(\text{OOH})_2]$ which yielded X-Ray quality crystals upon slow evaporation of a saturated heptane solution kept in a vial inside the glovebox.

B. Stopped-Flow Kinetic Measurements

Experimental: THF solutions of the reagents were prepared in a MBraun glovebox under Argon and placed in Hamilton gastight syringes. O₂ solutions were prepared by bubbling a 5% O₂/N₂ gas mixture into a syringe of dry THF and further diluted. Time-resolved spectra (400-650 nm) were acquired at temperatures from -90 to -75 °C using a Hi-Tech Scientific (Salisbury, Wiltshire, U.K.) SF-61DX2 Multi-Mixing CryoStopped-Flow Instrument and a J&M TIDASDAQ diode array detector with a Hi-Tech Scientific LHT50 tungsten lightsource. The stopped-flow instrument was equipped with stainless steel plumbing, a 1.00 cm³ stainless steel mixing cell with sapphire windows, and an anaerobic gas-flushing kit. The instrument was connected to a Dell computer with Kinetic Studio software (Hi-Tech Scientific). The temperature in the mixing cell was maintained to 0.1 °C, and the mixing time was 2-3 ms. The driving syringe compartment and the cooling bath, filled with ethanol (Fisher), were flushed with argon before and during the experiments, using anaerobic kit flush lines. All flow lines of the SF-61DX2 instrument were extensively washed with degassed, anhydrous toluene before charging the driving syringes with reactant solutions. The reactions were studied by rapid scanning spectrophotometry under stoichiometric conditions (1:1 molar ratio). All of the experiments were performed in a single-mixing mode of the instrument, with a 1:1 (v/v) mixing ratio. A series of three to six measurements at each temperature gave an acceptable standard deviation (within 10%). Data analysis was performed with Kinetic Studio software from Hi-Tech Scientific, IGOR Pro 5.0 by Wavemetrics, Inc. The kinetics of O₂ binding to [Pd(IPr)(P(*p*-tolyl)₃)] were measured in THF by stopped flow kinetic methods at very low temperature (-90 to -75 °C). The experiment was performed under stoichiometric conditions, with a 1:1 molar ratio of [Pd(IPr)(P(*o*-tolyl)₃)] to dioxygen. The O₂ solutions were prepared by bubbling a dilute O₂ gas mixture into THF (5%

O₂ /95% N₂) to saturation, and then further dilutions achieved a final concentration of 0.125 mM after mixing (for saturated O₂ /THF solutions, [O₂] = 10mM).¹ The rapid binding event was monitored by the decay of the [Pd(IPr)(P(*p*-tolyl)₃)] peak at λ= 414 nm over 2.5 seconds (Figure S5) with [Pd(IPr)(P(*p*-tolyl)₃)] = 0.122 mM after mixing.

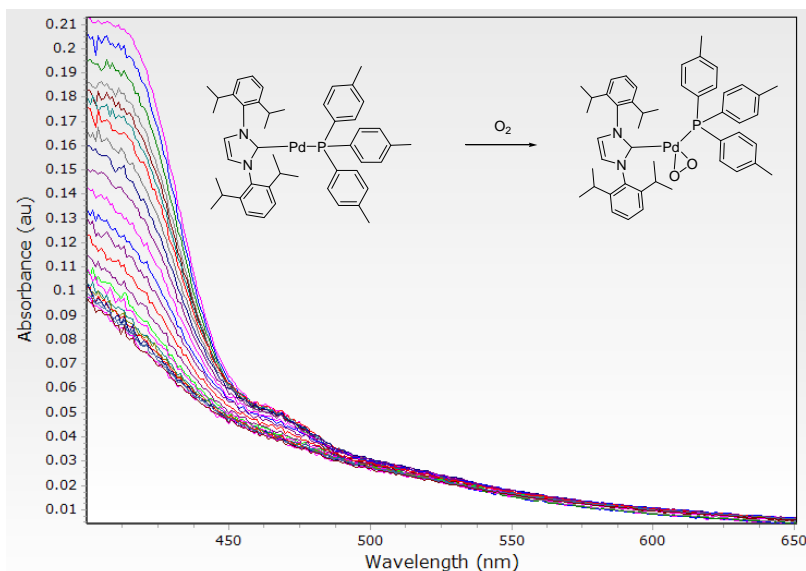


Figure S5. Diode array spectrum of O₂ (0.125mM) binding to [Pd(IPr)(P(*p*-tolyl)₃)] (0.122 mM) at -90 °C, all concentrations reported after mixing. Reaction kinetics were measured by monitoring the decay at λ = 414 nm.

The decay curves (Figure S6) for each temperature fit to a second order function under conditions where [A] = [B], shown in equation 1.

$$A_t = A_f - \left(\frac{(A_f - A_0)}{1 + (k^*[Pd]_0 * t)} \right) \quad \text{Eq 1}$$

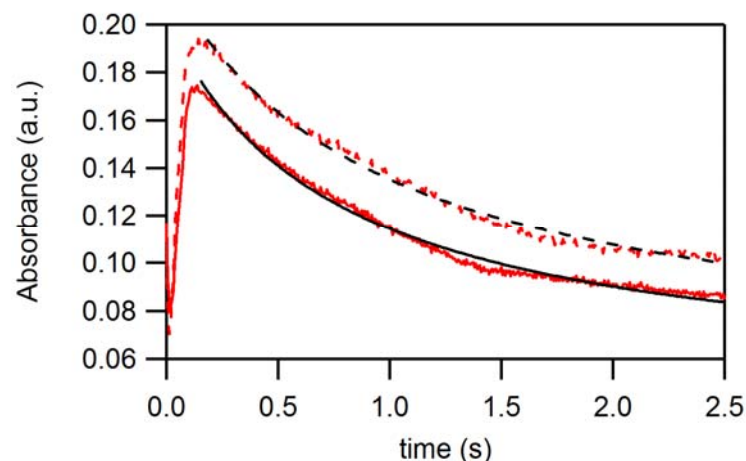


Figure S6. Decay curves (red) and second order fit curves (black) for -90 °C (dotted), and -85 °C (solid) with $[Pd] = [O_2] = 0.12$ M. Decay and growth under 0.2 s is due to mixing at low temperature and is not a feature of the reaction.

Second order rates were collected at each temperature and tabulated in Table S1. The temperature dependent rate constants measured in this work were extrapolated to 29 °C and yielded a rate, $k = 146,000 \text{ M}^{-1}\text{s}^{-1}$.

T (°C)	k_2 ($\text{M}^{-1}\text{s}^{-1}$)
-90	8,240
-85	10,700
-80	12,000
-75	14,300
29	146,000*

Table S1. Rate constants measured for O_2 binding with $[Pd(IPr)(P(p\text{-tolyl})_3)]$. Stopped-flow kinetics measured under stoichiometric conditions, $[Pd(IPr)(P(p\text{-tolyl})_3)] = 0.122$ mM and $[O_2] = 0.125$ mM. *Rate constant at 29 °C was extrapolated from low temperature measurements.

Activation parameters were obtained from the generated Eyring plot (Figure S7). The values obtained, $\Delta H^\ddagger = 2.2 \pm 0.3$ kcal/mol and $\Delta S^\ddagger = -28 \pm 2$ cal/molK, describe a small kinetic barrier and a binding step that is rate limiting.

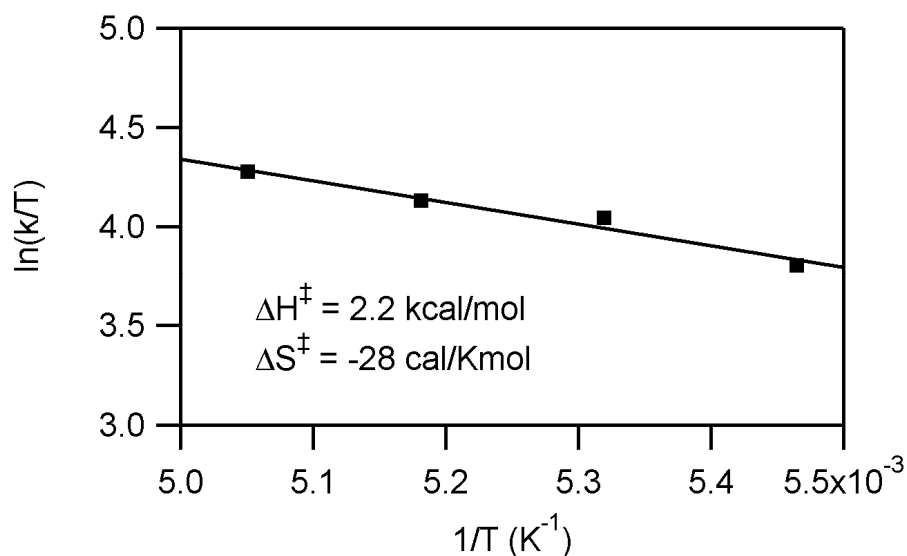


Figure S7. Eyring plot for O₂ binding with [Pd(IPr)(P(*p*-tolyl)₃)].

These data are combined with thermochemical data to generate a combined potential energy diagram shown in Figure S8.

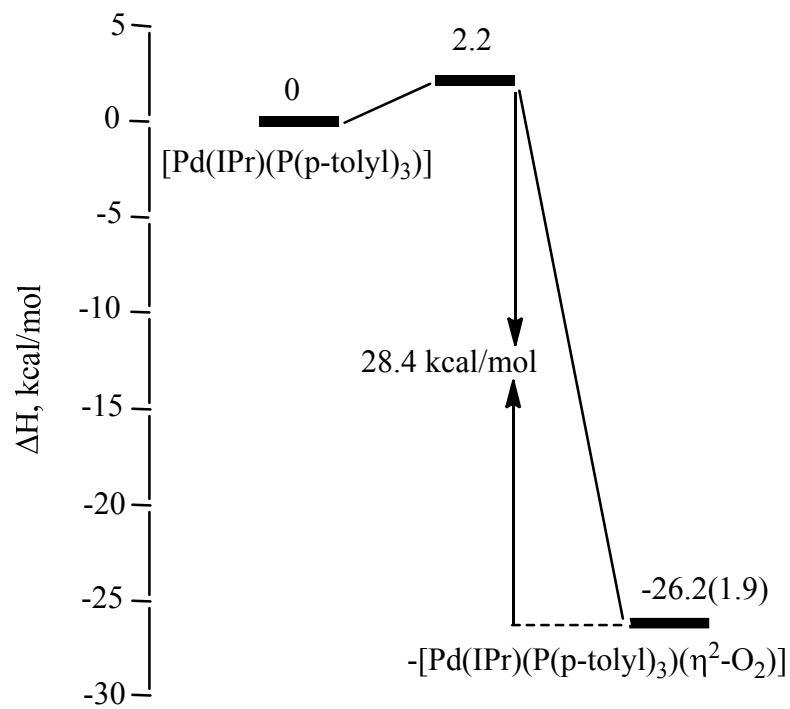


Figure S8. Potential Energy diagram (kcal/mol) derived for O₂ binding to [Pd(IPr)(P(*p*-tolyl)₃)].

C. Computational Details and Coordinates for **Ia**, **Ib**, and **Ic**

1. Computational methods and models. All calculations were performed using the Gaussian 03 program.⁴ The geometries of the structures were optimized in gas-phase without any symmetry constraints at the B3LYP/Lanl2dz level of theory using the Hay-Wadt effective core potential (ECP) for Pd.⁵ The available X-ray structures of the [Pd(IPr)₂(η^1 -O₂)] (**Ia**), [Pd(IMes)₂(η^1 -O₂)] (**Ib**) and [Pd (IPr)(PPh₃)(η^1 -O₂)] (**Ic**) complexes were utilized as the starting points for these calculations.

2. Cartesian coordinates (in Å) of the optimized structures.

[Pd(IPr)₂](n¹-O₂)] (Ia)

Pd	0.007011	0.021622	-0.039070
O	-0.124133	0.063087	-2.275290
O	-0.430003	-1.086221	-2.926142
C	0.522638	-2.008670	0.101634
N	1.725577	-2.639448	-0.218380
C	1.627308	-4.039770	-0.113245
H	2.460023	-4.689462	-0.322876
C	0.351365	-4.318163	0.280510
H	-0.138726	-5.255553	0.482456
N	-0.309916	-3.082914	0.411206
C	2.995401	-2.011913	-0.550077
C	3.404379	-1.958536	-1.907920
C	4.696557	-1.459815	-2.182244
H	5.037750	-1.407168	-3.212300
C	5.543721	-1.029077	-1.151452
H	6.534922	-0.647500	-1.386522
C	5.116401	-1.094835	0.183712
H	5.781927	-0.762095	0.975123
C	3.840201	-1.594837	0.513712
C	2.527389	-2.465765	-3.057711
H	1.499755	-2.564000	-2.695468
C	2.480695	-1.477932	-4.249336
H	2.131345	-0.493544	-3.925115
H	1.773274	-1.846289	-5.002308
H	3.461627	-1.368854	-4.732889
C	3.014581	-3.861095	-3.538236
H	2.997669	-4.601019	-2.727791
H	4.041976	-3.808484	-3.924103
H	2.367165	-4.229001	-4.345100
C	3.435156	-1.750877	1.983655
H	2.343109	-1.815463	2.030878
C	3.853500	-0.547330	2.859644
H	3.487064	0.394726	2.439750
H	4.944424	-0.475635	2.963158
H	3.437079	-0.660178	3.869799
C	4.017190	-3.070073	2.564826
H	3.677125	-3.944702	1.997133
H	3.703133	-3.200262	3.609458
H	5.115216	-3.054569	2.539237
C	-1.682272	-3.025629	0.885846
C	-1.909485	-2.952029	2.284561
C	-3.242511	-3.023535	2.740573
H	-3.446285	-2.970775	3.807321
C	-4.306927	-3.165742	1.837678
H	-5.328490	-3.222481	2.207077
C	-4.055263	-3.234798	0.459017
H	-4.886449	-3.340035	-0.232249
C	-2.740171	-3.170082	-0.048565
C	-0.771243	-2.823596	3.301833
H	0.173850	-2.738455	2.755628
C	-0.917594	-1.540381	4.158913
H	-0.950991	-0.650030	3.520665
H	-0.065418	-1.442218	4.845083
H	-1.833892	-1.563341	4.763456
C	-0.678132	-4.083241	4.203058
H	-0.529589	-4.991202	3.604470
H	-1.592511	-4.218408	4.795746
H	0.164971	-3.992943	4.901246
C	-2.486811	-3.312764	-1.551799
H	-1.483501	-2.937932	-1.774483
C	-3.465109	-2.468652	-2.402220
H	-3.161968	-2.510620	-3.455725
H	-3.450757	-1.419614	-2.091458
H	-4.497964	-2.838994	-2.334675
C	-2.558877	-4.807020	-1.973625
H	-2.359590	-4.904450	-3.048973
H	-3.554901	-5.225316	-1.772015

H	-1.821176	-5.417672	-1.437557
C	-0.514583	2.058056	-0.003622
N	-1.730693	2.662512	-0.324339
C	-1.652672	4.066025	-0.258081
H	-2.500304	4.696807	-0.465345
C	-0.372732	4.375416	0.099150
H	0.107660	5.325394	0.262645
N	0.308955	3.153364	0.249517
C	-2.984980	2.001543	-0.651580
C	-3.856713	1.649071	0.412115
C	-5.111873	1.099213	0.078770
H	-5.797676	0.810068	0.870063
C	-5.488521	0.922373	-1.260881
H	-6.461182	0.498391	-1.500312
C	-4.614104	1.292010	-2.293651
H	-4.917224	1.147505	-3.326266
C	-3.343422	1.839420	-2.016088
C	-3.503576	1.920076	1.878526
H	-2.416960	2.037556	1.952818
C	-4.159157	3.246719	2.355093
H	-3.836131	4.098736	1.744524
H	-3.888167	3.454615	3.399138
H	-5.253935	3.182499	2.294218
C	-3.899644	0.758814	2.819778
H	-3.487152	-0.193097	2.471591
H	-4.989650	0.650748	2.897832
H	-3.517777	0.952487	3.831369
C	-2.436349	2.291309	-3.166854
H	-1.409522	2.344210	-2.790289
C	-2.854703	3.705755	-3.660485
H	-2.808309	4.452201	-2.858228
H	-3.881243	3.693331	-4.051762
H	-2.188183	4.036362	-4.468275
C	-2.424670	1.302118	-4.357429
H	-2.129779	0.299614	-4.035632
H	-1.693026	1.639383	-5.103677
H	-3.401728	1.249702	-4.857542
C	1.706069	3.118896	0.641423
C	2.700972	3.091109	-0.370522
C	4.048520	3.165205	0.038420
H	4.835304	3.137841	-0.709379
C	4.390119	3.269629	1.396300
H	5.436037	3.329361	1.688880
C	3.386813	3.292594	2.376166
H	3.662782	3.368448	3.425199
C	2.023601	3.216746	2.019364
C	2.338548	3.040965	-1.858463
H	1.344843	2.590523	-1.952776
C	2.276623	4.477775	-2.449536
H	1.542478	5.102188	-1.926151
H	1.992146	4.438736	-3.509401
H	3.255864	4.970962	-2.377623
C	3.305986	2.165975	-2.687755
H	3.403501	1.164508	-2.257589
H	4.307170	2.613132	-2.758300
H	2.920643	2.061023	-3.709950
C	0.951603	3.239436	3.113995
H	-0.032918	3.181455	2.637375
C	0.995895	4.557759	3.929660
H	0.866379	5.433886	3.281114
H	1.951684	4.670696	4.457786
H	0.194843	4.567914	4.680821
C	1.079042	2.006671	4.045839
H	1.007082	1.076699	3.470379
H	0.276488	2.012526	4.795776
H	2.038841	2.005902	4.579158

[Pd(IMes)₂(η¹-O₂)] (Ib)

Pd	0.001717	0.013488	-0.005677
O	-0.448671	-0.934571	-2.962527
O	0.106851	0.076247	-2.252312
N	-0.913913	-2.907308	0.627032
N	1.168703	-2.914412	0.000727
N	0.915050	2.993876	0.323742
N	-1.171570	2.915362	-0.283681
C	0.102601	-2.051441	0.222785
C	-0.490483	-4.249724	0.654017
H	-1.146532	-5.054802	0.941197
C	0.819000	-4.253698	0.260673
H	1.520873	-5.063104	0.145448
C	-2.259718	-2.501573	0.976386
C	-2.544959	-2.159826	2.319011
C	-3.871775	-1.830577	2.653231
H	-4.106229	-1.568669	3.683930
C	-4.900188	-1.833313	1.686830
C	-4.573401	-2.170020	0.359311
H	-5.353185	-2.168479	-0.399833
C	-3.257287	-2.503854	-0.023630
C	-1.450220	-2.127759	3.368081
H	-1.858628	-1.867850	4.350825
H	-0.685154	-1.385556	3.103853
H	-0.939503	-3.095728	3.456592
C	-6.321885	-1.464686	2.072099
H	-6.407896	-0.389840	2.288375
H	-6.645842	-2.002069	2.972909
H	-7.028331	-1.697869	1.267452
C	-2.928985	-2.840542	-1.464401
H	-2.183832	-2.148454	-1.878463
H	-3.828540	-2.789459	-2.087684
H	-2.510110	-3.852087	-1.558601
C	2.494860	-2.528657	-0.440172
C	2.856276	-2.735562	-1.791675
C	4.172323	-2.409315	-2.179822
H	4.463030	-2.560658	-3.217592
C	5.110906	-1.889243	-1.267536
C	4.712335	-1.704628	0.071981
H	5.425743	-1.309950	0.793310
C	3.410596	-2.015923	0.507735
C	1.871191	-3.281129	-2.806586
H	1.495553	-4.272659	-2.520307
H	2.343544	-3.371467	-3.790888
H	1.002041	-2.619090	-2.904931
C	6.511492	-1.514427	-1.718289
H	6.792365	-2.041337	-2.637571
H	7.258301	-1.750202	-0.949675
H	6.583064	-0.436005	-1.923181
C	3.009284	-1.794864	1.952627
H	2.597996	-2.707133	2.405283
H	2.233891	-1.021041	2.020060
H	3.868760	-1.472338	2.550139
C	-0.100424	2.090736	0.037218
C	0.485384	4.328184	0.185595
H	1.140060	5.165583	0.362544
C	-0.827170	4.277625	-0.195235
H	-1.533034	5.063425	-0.408387
C	2.269741	2.642567	0.695756
C	3.222294	2.404989	-0.322010
C	4.551260	2.147539	0.067619
H	5.296643	1.966976	-0.704900
C	4.937139	2.111683	1.423130
C	3.953748	2.335525	2.407879
H	4.232457	2.304903	3.459702
C	2.612266	2.598740	2.065737
C	2.828266	2.408130	-1.785575
H	3.710157	2.292953	-2.425045

H	2.320680	3.339704	-2.069319
H	2.135480	1.586109	-2.006888
C	6.374377	1.815128	1.812381
H	6.603888	2.187929	2.817411
H	7.082629	2.272494	1.110533
H	6.568936	0.732413	1.810487
C	1.564629	2.806248	3.142929
H	1.072390	3.783540	3.055335
H	2.012187	2.739969	4.140433
H	0.777389	2.044467	3.066848
C	-2.491335	2.468924	-0.686539
C	-2.801326	2.407200	-2.065389
C	-4.107615	2.027922	-2.431048
H	-4.358902	1.971862	-3.488593
C	-5.086128	1.706454	-1.468558
C	-4.736288	1.778518	-0.105854
H	-5.478993	1.533035	0.650942
C	-3.443236	2.153974	0.308361
C	-1.760946	2.711107	-3.125152
H	-1.324510	3.710777	-2.998685
H	-2.201653	2.657308	-4.126382
H	-0.942210	1.982658	-3.072352
C	-6.475273	1.266346	-1.894510
H	-6.815849	1.813965	-2.781887
H	-7.209619	1.422797	-1.095448
H	-6.486003	0.196322	-2.148753
C	-3.085233	2.193167	1.780805
H	-3.973776	2.038257	2.402389
H	-2.627909	3.149377	2.066754
H	-2.360689	1.402837	2.016557

[Pd (IPr)(PPh₃)(η^1 -O₂)] (Ic)

Pd	0.068326	-0.154333	-0.188150
C	-1.953428	0.187965	0.087990
N	-3.005189	-0.718497	0.117054
P	2.527647	-0.356441	-0.078771
C	-4.248832	-0.066338	0.217069
H	-5.180149	-0.606035	0.257964
N	-2.590726	1.420443	0.177006
C	-3.988746	1.275775	0.255324
H	-4.651742	2.120836	0.336095
C	-2.871231	-2.166655	0.142230
C	-2.711802	-2.806047	1.398784
C	-2.627623	-4.214349	1.414783
H	-2.499935	-4.731940	2.362298
C	-2.708464	-4.955617	0.226866
H	-2.644314	-6.040931	0.257921
C	-2.870500	-4.298816	-1.002608
H	-2.925324	-4.882337	-1.916900
C	-2.951409	-2.892015	-1.074925
C	-2.625588	-2.034742	2.719828
H	-2.733930	-0.965799	2.507507
C	-1.240500	-2.227740	3.389856
H	-1.064877	-3.281001	3.646498
H	-1.178435	-1.640296	4.315881
H	-0.437559	-1.898181	2.720437
C	-3.772031	-2.431927	3.686272
H	-4.755763	-2.263407	3.229159
H	-3.716284	-1.837169	4.607852
H	-3.711122	-3.491062	3.968130
C	-3.155572	-2.201066	-2.425805
H	-2.856116	-1.153029	-2.329041
C	-2.274486	-2.806664	-3.545214
H	-1.219550	-2.818558	-3.250166
H	-2.357832	-2.192217	-4.449581
H	-2.579810	-3.829932	-3.803798
C	-4.654374	-2.241933	-2.835153
H	-4.799167	-1.723213	-3.791885
H	-5.292498	-1.755283	-2.086228
H	-5.002045	-3.277579	-2.952924
C	-1.922508	2.708181	0.276093
C	-1.762996	3.498924	-0.892167
C	-1.160219	4.766586	-0.745215
H	-1.024671	5.394595	-1.620841
C	-0.726496	5.225543	0.508259
H	-0.264948	6.206498	0.597802
C	-0.891585	4.422275	1.646219
H	-0.551862	4.784619	2.613261
C	-1.497050	3.150724	1.556020
C	-2.252205	3.037212	-2.267992
H	-2.362147	1.948737	-2.248409
C	-3.637525	3.664289	-2.589072
H	-4.390376	3.392949	-1.838017
H	-3.993924	3.313781	-3.566618
H	-3.574404	4.760670	-2.622767
C	-1.243265	3.355734	-3.398219
H	-1.146586	4.436176	-3.573748
H	-1.582583	2.893732	-4.333044
H	-0.253669	2.945746	-3.169809
C	-1.671293	2.314736	2.828027
H	-2.155524	1.369745	2.561041
C	-2.589306	3.032484	3.852472
H	-2.151341	3.981818	4.187193
H	-2.736999	2.401149	4.738813
H	-3.574326	3.252020	3.420302
C	-0.300263	1.960575	3.460159
H	0.325571	1.410670	2.747529
H	-0.441787	1.331488	4.349238
H	0.243780	2.862609	3.769464

C	3.381330	1.249890	-0.573851
C	2.631479	2.444184	-0.508553
H	1.589008	2.409165	-0.199230
C	3.220650	3.673211	-0.861128
H	2.629935	4.584512	-0.809632
C	4.560212	3.716850	-1.291980
H	5.013707	4.664913	-1.572654
C	5.308121	2.525325	-1.371702
H	6.339749	2.550365	-1.715237
C	4.721620	1.297035	-1.013189
H	5.301889	0.381620	-1.093600
C	3.204322	-0.711790	1.646765
C	4.116387	0.136902	2.306660
H	4.484255	1.031887	1.813210
C	4.554947	-0.165431	3.611747
H	5.256156	0.500171	4.110010
C	4.091163	-1.320969	4.266812
H	4.431824	-1.554196	5.273012
C	3.177251	-2.172101	3.612533
H	2.808242	-3.065020	4.111764
C	2.731837	-1.864923	2.315165
H	2.015092	-2.519879	1.823563
C	3.396705	-1.650583	-1.143877
C	2.880986	-1.887686	-2.438300
H	2.000416	-1.348400	-2.778995
C	3.503019	-2.825783	-3.283002
H	3.099288	-3.000652	-4.277504
C	4.634917	-3.539852	-2.843233
H	5.110435	-4.267942	-3.496756
C	5.144479	-3.311176	-1.550907
H	6.015367	-3.861360	-1.201512
C	4.529639	-2.368129	-0.704424
H	4.928594	-2.205794	0.293451
O	0.137962	-0.153722	-2.422392
O	-0.956288	0.143800	-3.144477

D. Structural Data for Compounds 3 and 5.

Crystallographic Analyses for Compound 3: Very small single crystals of **3** suitable for diffraction analysis were grown by slow evaporation of solvent from a hexane solution at room temperature in a dry box. X-ray diffraction studies were performed at 93K using a Rigaku MM007/Mercury/ diffractometer (confocal optics Mo-K α radiation) Intensity data were collected using ω and ϕ steps accumulating area detector frames spanning a hemisphere of reciprocal space (data were integrated using CrystalClear⁶). All data were corrected for Lorentz, polarisation and long-term intensity fluctuations. Absorption effects were corrected on the basis of multiple equivalent reflections. The structure was solved by direct methods and refined by full-matrix least-squares against F^2 (SHELXTL⁷). All hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealised geometries. The R factor reflects the very small crystal size and the presence of half a hexane solvate molecule.

Crystallographic Analyses for Compound 5: Single crystals of **5** suitable for diffraction analysis were grown by slow evaporation of solvent from a heptane solution at room temperature in a dry box. The data crystal of compound **5** was glued onto the end of a thin glass fiber. X-ray intensity data were measured by using a Bruker SMART APEX2 CCD-based diffractometer using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$).⁸ The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm.⁸ Corrections for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS. All structures were solved by a combination of direct methods and difference Fourier syntheses,

and refined by full-matrix least-squares on F^2 , by using the SHELXTL software package.⁹ Crystal data, data collection parameters, and results of the analyses are listed in Table S2.

Compound **5** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms during the least-squares refinements.

Table S2. Crystallographic Data for Compounds 3 and 5.

	3	5
Empirical formula	PdO ₄ N ₄ C ₅₄ H ₇₂ •½C ₆ H ₁₄	PdO ₄ N ₄ C ₅₄ H ₇₈
Formula weight	990.64	953.60
Crystal system	Monoclinic	Triclinic
Lattice parameters		
<i>a</i> (Å)	13.766(4)	12.2884(5)
<i>b</i> (Å)	15.624(4)	12.3340(5)
<i>c</i> (Å)	25.915(8)	17.2479(7)
α (deg)	90	82.982(1)
β (deg)	103.647(7)	87.966(1)
γ (deg)	90	89.015(1)
<i>V</i> (Å ³)	5416(3)	2592.74(18)
Space group	<i>P</i> 2 ₁ / <i>c</i> (# 14)	<i>P</i> $\bar{1}$ (#2)
Z value	4	2
ρ _{calc} (g / cm ³)	1.215	1.221
μ (Mo Kα) (mm ⁻¹)	0.389	0.404
Temperature (K)	93	296
2Θ _{max} (°)	50.00	57.00
No. Obs. (<i>I</i> > 2σ(<i>I</i>))	6664	10468
No. Parameters	595	586
Goodness of fit	1.138	1.021
Max. shift in cycle	0.013	0.001
Residuals*:R1; wR2	0.1261; 0.2906	0.0375; 0.0848
Absorption Correction, Max/min	Multi-scan 1.0000/0.9488	Multi-scan 0.7465/0.6552
Largest peak in Final Diff. Map (e ⁻ / Å ³)	3.271	0.597

$$*R = \sum_{hkl} (|F_{obs}| - |F_{calc}|) / \sum_{hkl} |F_{obs}|; R_w = [\sum_{hkl} w(|F_{obs}| - |F_{calc}|)^2 / \sum_{hkl} w F_{obs}^2]^{1/2},$$

$$w = 1/\sigma^2(F_{obs}); GOF = [\sum_{hkl} w(|F_{obs}| - |F_{calc}|)^2 / (n_{data} - n_{vari})]^{1/2}.$$

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