O–O Activation

Dimetallic Dioxygen Activation Leading to a Doubly Oxygen-Bridged Dirhodium Complex**

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Catalytic oxygenation constitutes an important method of converting readily available alkenes into chemicals with high added value. These oxygenations should preferably use the cheap and environmentally benign dioxygen as oxidant, and incorporate both oxygen atoms into the substrate molecules, thus optimizing atom economy.[1] However, with the exception of the Wacker process, such practical use of oxygen seems nowadays restricted to a few heterogeneous catalysts,[2]

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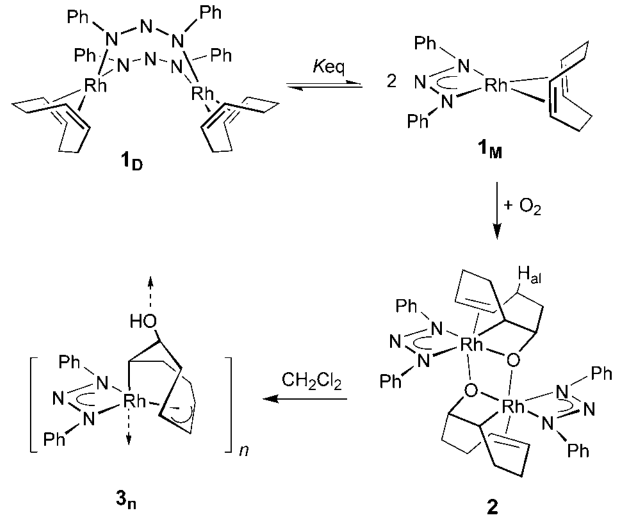
although important progress towards this goal has been reported in the chemistry of soluble metal complexes.[3]

A recent review by Gal and co-workers[4] analyzes in detail the reactivity of rhodium and iridium complexes relevant to alkene oxygenation. Often, the use of peroxides as oxidants leads to facile monooxygenation reactions, through C–O bond-forming steps, to afford reactive 2-metallaoxetane intermediates.[5–7] In contrast, the more scarce C–O bond-forming reactions using dioxygen are assumed to involve the initial formation of 3-metalla-1,2-dioxolanes,[8] from which the evolution to oxygenated products seems to follow unselective routes and most often requires the presence of sacrificial reductants.[4] An exception to this inconvenient behavior has been reported for the 1,5-cyclooctadiene dianionic complex $[Ir(P_3O_9)(C_8H_{12})]^{2-}$, in which the formation of a 2-metallaoxetane intermediate from 0.5 molar equivalents of dioxygen has been suggested to be the consequence of a dimetallic O–O bond cleavage.[9] Herein we provide further evidence for the feasibility of this atom-economic dimetallic oxygenation route, by describing the facile formation of a dinuclear 2-metallaoxetane compound from dioxygen and an equilibrium mixture of the mono- and dinuclear rhodium complexes $[Rh(PhN_3Ph)(C_8H_{12})]$ ($\mathbf{1_M}$) and $[\{Rh(\mu\text{-}PhN_3Ph)(C_8H_{12})\}_2]$ ($\mathbf{1_D}$).

The bis(phenyl)triazenide rhodium(I) compound $[\{Rh(PhN_3Ph)(C_8H_{12})\}_n]$ (**1**), first reported by Knoth,[10] was easily prepared by treating $[\{Rh(\mu\text{-}OMe)(C_8H_{12})\}_2]$ with bis(phenyl)triazene in toluene. By comparison with rhodium triazenide compounds previously characterized by X-ray diffraction studies,[11] it was likely that the red solid obtained from the reaction was a dinuclear compound with bridging triazenide ligands. However, the NMR spectra of the compound dissolved in [D$_6$]benzene is indicative of an equilibrium mixture of the mono- and dinuclear complexes shown in Scheme 1. The dissociation equilibrium constant K_{eq} was estimated by NMR spectroscopic analysis to be 0.092 mol L^{-1} at 293 K.



Scheme 1. Equilibration between the mono- and dinuclear complexes, and the products of the reaction of **1** with dioxygen.

Exposure of **1** to dioxygen in toluene at 293 K and atmospheric pressure gave the dinuclear dirhodadioxetane complex $[\{Rh(PhN_3Ph)(OC_8H_{12})\}_2]$ (**2**, Scheme 1) in 90% yield. Volumetric gas-burette measurements with O_2 indicated a consumption of 0.5 molecules of gas per atom of rhodium (0.51 ± 0.03 equiv), thus showing that all the reacting dioxygen was incorporated into **2**. The molecular structure of complex **2** (Figure 1)[12] confirms that, despite the presence of potentially bridging triazenide ligands, the dinuclear structure is held by bridging oxygen atoms—a feature by itself suggestive of a dimetallic activation of dioxygen. Moreover, among the few 2-metallaoxetane moieties resulting from insertion of oxygen atoms into metal–alkene bonds,[5,6,9] compound **2** constitutes the first example of a bridging one.

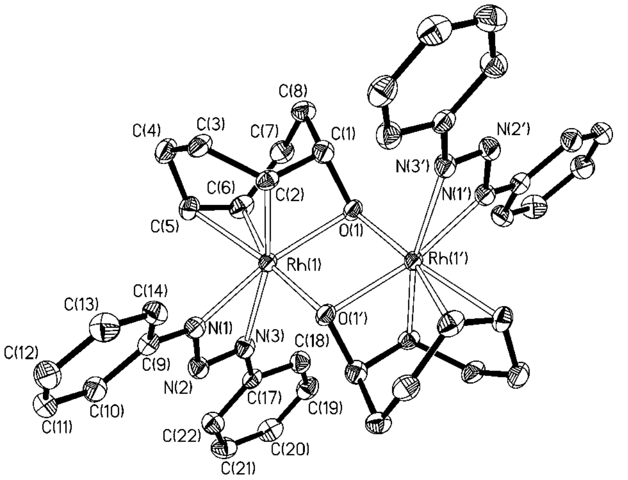


Figure 1. Solid-state structure of the dinuclear complex **2**. Selected bond distances [Å] and angles [°]: Rh(1)-N(1) 2.040(3), Rh(1)-N(3) 2.347(3), Rh(1)-O(1) 2.076(3), Rh(1)-O(1′) 2.064(3), Rh(1)-C(2) 2.037(4), Rh(1)-C(5) 2.223(4), Rh(1)-C(6) 2.206(4); N(1)-Rh(1)-O(1) 167.42(11), N(3)-Rh(1)-C(2) 167.62(13), O(1′)-Rh(1)-C(5) 162.51(12).

Complex **2** was found to be kinetically unstable in solution, slowly evolving to $[\{Rh(PhN_3Ph)(HO\text{-}C_8H_{11})\}_n]$ ($\mathbf{3_n}$, Scheme 1). The transformation was found to be complete in about three days at room temperature in dichloromethane. As confirmed by the solid-state structure shown in Figures 2 and 3,[13] the transformation involves the isomerization of the (η^2-

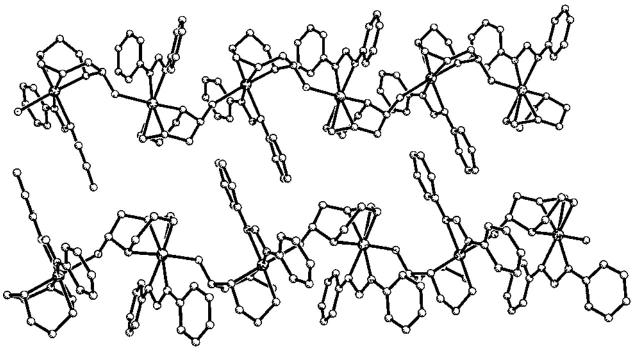


Figure 2. Polymeric chains formed in the crystal structure of complex $\mathbf{3_n}$ by the two independent dimeric units.

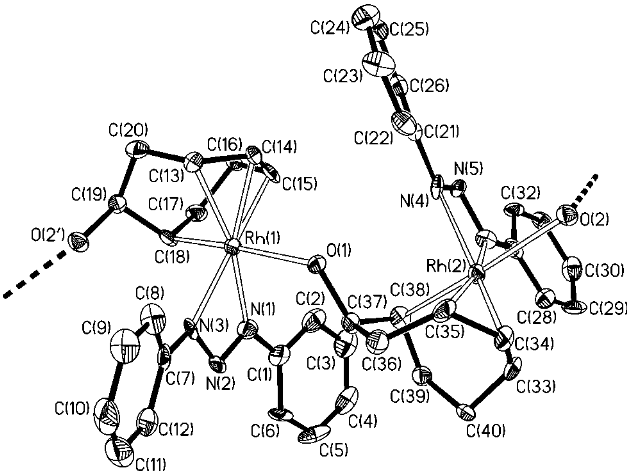


Figure 3. Solid-state structure of one of the two independent dimeric moieties of $\mathbf{3_n}$. Selected bond distances [Å] and angles [°] (mean values for the four equivalent parameters)[11]: Rh-N(1) 2.121(4), Rh-N(3) 2.139(4), Rh-O(1) 2.359(3), Rh-C(18) 2.051(5), Rh-C(13) 2.163(5), Rh-C(14) 2.080(5), Rh-C(15) 2.163(5); N(1)-Rh-C(13) 168.8(2), N(3)-Rh-C(15) 170.4(2), O(1)-Rh-C(18) 175.8(2).

κ-O,C-OC_8H_{12}) ligand of **2** into a hydroxyallyl (η^3-κ-C-(HO)C_8H_{11}) isomeric ligand (Scheme 1). Such an isomerization has been proposed to involve a metal-mediated activation of an allylic C–H bond followed by the transfer of the activated hydrogen atom to the alkoxy oxygen atom.[5,6,9]

The solid-state structure of $\mathbf{3_n}$ consists of a polymeric chain of mononuclear complexes (Figure 2) connected by Rh–O bonds (mean Rh–O(1) bond lengths 2.359(3) Å). Such bonds are long and presumably fragile, since they take place at a rhodium coordination position strongly labilized by the large *trans* effect of a σ-sp^3 carbon atom. Therefore, it seems unlikely that such a polymeric structure could remain in solution.

Accordingly, the NMR spectra of solutions of $\mathbf{3_n}$ are indicative of two equivalent phenyl groups, a feature hardly compatible with the polymeric structure, but likely for a potentially fluxional 16-electron Rh^{III} fragment.

The dioxygen activation reaction leading to complex **2** has been investigated kinetically by O_2-uptake experiments on solutions of **1** in toluene at 293 K. The initial concentrations of **1** in these solutions, expressed as concentrations of rhodium atoms $[Rh]_0$, were about 5×10^{-3} molL^{-1}. At these concentrations and below, the equilibrium between $\mathbf{1_D}$ and $\mathbf{1_M}$ is greatly shifted toward the mononuclear compound, so that the concentration of $\mathbf{1_M}$ approaches a linear dependence upon that of rhodium, namely $[\mathbf{1_M}]\approx[Rh]$. In turn, that of $\mathbf{1_D}$ is better described by the expression of the equilibrium constant, namely $[\mathbf{1_D}]\approx[Rh]^2/K_{eq}$, thus depending upon the square of the rhodium concentration. Figure 4 and Table 1 shows examples for the reaction profiles obtained under constant pressure of dioxygen, which correspond well to those expected for a first-order dependence upon complex concentration. The logarithmic representation of the initial reaction rates (v_0) versus $[Rh]_0$ indicates a linear dependence, therefore confirming the mononuclear complex $\mathbf{1_M}$, rather than $\mathbf{1_D}$, to be the kinetically relevant species in this oxygenation. The dependence of the pseudo-first-order rate constants k_{obs} upon dioxygen pressure confirms that the oxygenation rate is also first order in dioxygen.

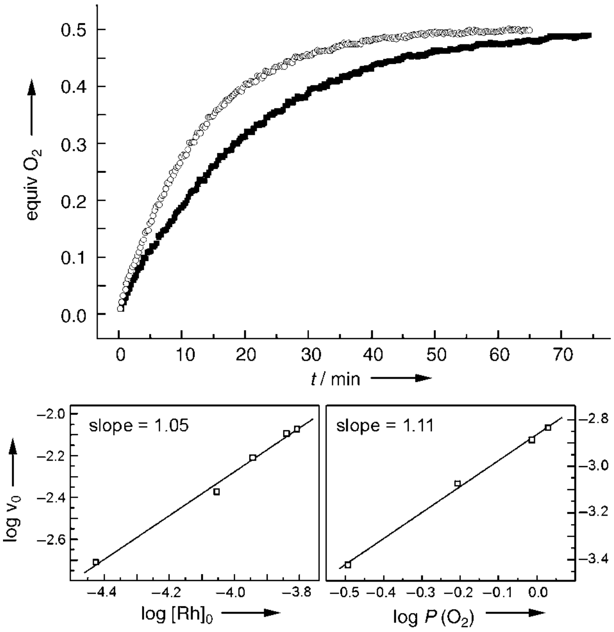
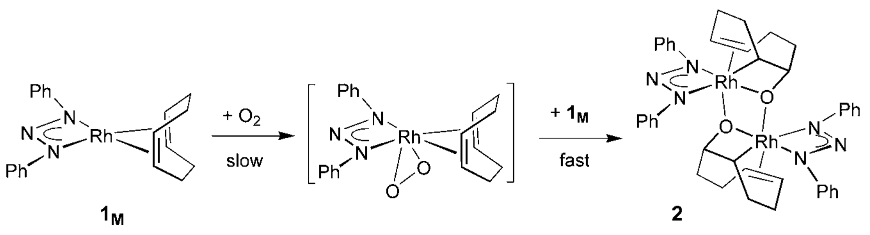


Figure 4. Top: Examples of O_2 uptake experiments in solutions of **1** in toluene ($[Rh]_0=6.18\times10^{-3}$ molL^{-1}) at 293 K; ○: $P=1.00$ bar; ■: $P=0.65$ bar. Bottom: Dependence of the initial reaction rates upon the initial concentration of **1** (left) and dependence of the pseudo-first-order rate constants k_{obs} upon the O_2 partial pressure (right).

Table 1: Kinetic data for the reaction of **1** with dioxygen.

$[Rh]_0$ [$\times10^{-3}$ M]	$P(O_2)$ [bar]	v_0 [mmol O_2 s^{-1}]	k_{obs} [$\times10^{-3}$ s^{-1}]
8.48	0.97	1.56×10^{-4}	1.34
8.08	0.97	1.45×10^{-4}	1.27
6.18	0.97	1.14×10^{-4}	1.29
4.24	0.97	8.84×10^{-5}	1.28
1.94	0.97	3.76×10^{-5}	1.27
8.08	1.07	3.76×10^{-5}	1.43
8.08	0.62	3.76×10^{-5}	0.83
8.08	0.32	3.76×10^{-5}	0.37

These kinetic data discount any mechanism initiated by reaction of dioxygen with the dinuclear complex $\mathbf{1_D}$, and evidence a reaction of dioxygen with the mononuclear complex $\mathbf{1_M}$ as the most likely rate-determining step in the process (Scheme 2). This conclusion is compatible with the mechanism previously proposed by Klemperer and co-workers for the aforementioned singular example of dioxygen activation.[9] Adaptation of this proposal to our reaction in Scheme 2 would result in a mononuclear complex coordinating dioxygen, which undergoes the attack by an intact mononuclear complex ($\mathbf{1_M}$) to complete a dimetallic dioxygen cleavage. In our system, such a dimetallic activation step seems to be fast; likely as a consequence of the unsaturated character of the triazenide–rhodium complex $\mathbf{1_M}$. The coordination requirements of the Klemperer's tridentate $P_3O_9^{3-}$ ancillary ligand were proposed to favor the splitting of the



Scheme 2. Proposed mechanism for the reaction of dioxygen with **1**.

dinuclear species resulting after dioxygen activation, a feature not required in our triazenide oxygenation product, which remains dinuclear (Scheme 2).

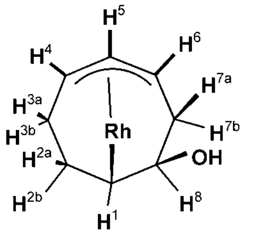
Although the above mechanism could be within the reach of other unsaturated mononuclear complexes or fragments, our preliminary investigation of rhodium compounds isoelectronic and very closely related to **1** indicates that this dioxygen activation is far from general. Actually, the complex [{Rh(μ-PhNCHNPh)(C_8H_{12})}$_2$],[13] which remains dinuclear at all concentration ranges, did not undergo reaction with dioxygen under the conditions described for **1**, while the mononuclear species [Rh(PhNC(Ph)NPh)(C_8H_{12})],[14] which does not form detectable dimers in solution, did not activate dioxygen either. These observations might suggest a correlation between the ability of unsaturated mononuclear fragments to reversibly form dinuclear species in solution and its activity in these dioxygen cleavage reactions. Whether or not this correlation exists is currently being investigated within our search for oxygenation catalysts, which can benefit from such facile, selective, and atom-economic dioxygen dimetallic activation.

Experimental Section

1: The addition of PhNNNHPh (165.7 mg, 0.84 mmol) to a yellow solution of [{Rh(μ-OMe)(cod)}$_2$] (203.4 mg, 0.42 mmol; cod = cycloocta-1,5-diene) in toluene (10 mL) produced a red solution from which a red solid precipitated in a few minutes. Hexane (5 mL) was added after 30 min to complete the precipitation of the solid. The solid was filtered under argon, washed with hexane (2 × 4 mL), and vacuum-dried. Yield: 290.8 mg (85 %). Elemental analysis (%) calcd for $C_{20}H_{22}N_3Rh$: C 58.97, H 5.44, N 10.32; found: C 59.19, H 5.34, N 10.31; ^{1}H NMR ([D$_6$]benzene, 25 °C) for $\mathbf{1_M}$: $\delta = 7.33$ (br d, J(H,H) = 7.7 Hz, 4 H), 7.14 (t, J(H,H) = 6.9 Hz, 4 H) and 6.93 (tt, J(H,H) = 7.4, 1.1 Hz, 2 H; C_6H_5), 4.32 (br s, 4 H, =CH), 2.05 (m, 4 H, CH_2^{exo}), 1.36 (q, J(H,H) = 7.9 Hz, 4 H, CH_2^{endo}); for $\mathbf{1_D}$: $\delta = 7.77$ (br s, 8 H), 7.23 (t, J(H,H) = 8.3 Hz, 8 H) and 7.03 (tt, J(H,H) = 7.4, 1.1 Hz, 4 H; C_6H_5), 4.64 (br s, 4 H) and 4.11 (br s, 4 H; =CH), 2.76 (m, 4 H) and 2.18 (m, 4 H; CH_2^{exo}), 1.70 (q, J(H,H) = 7.7 Hz, 4 H) and 1.47 (q, J(H,H) = 7.9 Hz, 4 H; CH_2^{endo}); ^{13}C{^{1}H} NMR ([D$_6$]benzene, 25 °C) for $\mathbf{1_M}$: $\delta =$ 149.5 (C^{ipso}-C_6H_5), 129.2 (C^{meta}-C_6H_5), 124.1 (C^{para}-C_6H_5), 117.2 (C^{ortho}-C_6H_5), 80.3 (d, J(C,Rh) = 12 Hz, =CH), 30.6 (CH); for $\mathbf{1_D}$: $\delta = 152.9$ (C^{ipso}-C_6H_5), 128.4 (C^{meta}-C_6H_5), 124.9 (C^{para}-C_6H_5), 124.1 (C^{ortho}-C_6H_5), 87.6 (br) and 76.8 (br; =CH), 31.1 and 30.8 (CH); MS: *m/z* (%): 814 (20) [M^+] ($\mathbf{1_D}$), 407 (100) [M^+] ($\mathbf{1_M}$).

2: A suspension of [{Rh(PhNNNPh)(C_8H_{12})}$_n$] (150.0 mg) in toluene (8 mL) was stirred in an oxygen atmosphere for 2 h. The initial dark red suspension evolved to an orange solution, which was concentrated to about 3 mL. Hexane (15 mL) was added to complete the precipitation of the solid, which was filtered off, washed with hexane (2 × 5 mL), and vacuum-dried. Yield: 156 mg (90 %). Elemental analysis (%) calcd for $C_{40}H_{44}N_6O_2Rh_2$: C 56.75, H 5.24, N 9.93; found: C 57.01, H 5.03, N 9.79; ^{1}H NMR (CDCl$_3$, 25 °C) (assigned from ^{1}H,^{1}H-COSY spectrum) $\delta = 7.47$ (m, 8 H, H^{ortho}-C_6H_5), 7.36 (t, J(H,H) = 7.5 Hz, 4 H) and 7.32 (t, J(H,H) = 8.2 Hz, 4 H; H^{meta}-C_6H_5), 7.11 (t, J(H,H) = 7.3 Hz, 2 H) and 7.04 (t, J(H,H) = 7.2 Hz, 2 H; H^{para}-C_6H_5), 6.25 (t, J(H,H) = 7.4 Hz, 2 H) and 5.00 (m, 2 H; =CH), 5.25 (t, J(H,H) = 6.9 Hz, 2 H; HC-O-Rh), 4.78 (m, 2 H; HC-Rh), 2.62 (m, 2 H), 2.38 (m, 2 H), 1.91 (m, 8 H), 1.50 (m, 2 H) and 0.80 (m, 2 H; CH$_2$); ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C) $\delta = 149.6$ and 148.4 (C^{ipso}-C_6H_5), 129.1 and 128.6 (C^{meta}-C_6H_5), 123.7 and 123.3 (C^{para}-C_6H_5), 119.2 and 117.7 (C^{ortho}-C_6H_5), 100.5 (d, J(C,Rh) = 8 Hz) and 95.7 (d, J(C,Rh) = 7 Hz; =CH), 94.6 (d, J(C,Rh) = 2 Hz; HC-O-Rh), 33.6 (d, J(C,Rh) = 17 Hz; HC-Rh), 33.9, 27.8, 24.8 and 20.6 (CH$_2$); MS: *m/z* (%): 847 (12) [M^+], 423 (100) [$(M/2)^+$].

3: An orange solution of **2** (100 mg, 0.12 mmol) in CH$_2$Cl$_2$ (10 mL) became green over 72 h in an argon atmosphere. Concentration of the solution to about 2 mL and addition of hexane (10 mL) afforded the product as a green solid, which was separated by filtration and dried under vacuum. Yield: 70 mg (70 %). Elemental analysis (%) calcd for $C_{20}H_{22}N_3O_1Rh_1$: C 56.75, H 5.24, N 9.93; found: C 56.85, H 5.23, N 9.75; ^{1}H NMR (CDCl$_3$, 25 °C): (assigned from ^{1}H,^{1}H-COSY spectrum) $\delta = 7.56$ (d, J(H,H) = 7.8 Hz, 4 H; H^{ortho}-C_6H_5), 7.34 (t, J(H,H) = 7.8 Hz, 4 H; H^{meta}-C_6H_5), 7.06 (t, J(H,H) = 7.2 Hz, 2 H; H^{para}-C_6H_5), 5.15 (m, 2 H; H^4 and H^6), 4.01 (t, J(H,H) = 8.7 Hz, 1 H; H^5), 3.52 (m, 1 H; H^1), 2.68 (m, 1 H; H^8), 2.36 (d, J(H,H) = 9.0 Hz, 1 H; OH), 2.03 (m, 3 H; H^{2a}, H^{3a}, H^{7a}), 1.32 (m, 1 H; H^{7b}), 1.27 (m, 1 H; H^{3b}), 0.67 (m, 1 H; H^{2b}); MS: *m/z* (%): 423 (100) [M^+].



Kinetic measurements: Dioxygen uptake experiments were performed in an apparatus consisting of a (7.99 mL) stainless-steel gas reservoir triply connected to a high-pressure dioxygen source, a pressure transmitter, and an electronic pressure meter/controller (EL-Press, Bronkhorst HI-TEC). The outlet of the pressure controller was connected to a 100-mL reaction flask, also connected to a Schlenk manifold to allow for manipulation of the reaction and degassing. In a typical reaction, a solution of **1** at the desired concentration in toluene was transferred to the reaction flask, degassed in vacuo over 30 s, and then exposed to dioxygen at the desired total pressure. The pressure was programmed at the computer connected to the pressure controller. The reaction flask was shaken vigorously during reaction. Consumption of dioxygen was registered as a pressure decrease in the closed reservoir, by means of the pressure transmitter, at intervals of 15 s. The pressure decrease was converted into the moles of dioxygen consumed by using the precalibrated volume of the reservoir and considering an ideal gas behavior. Initial rates were obtained through a least-square fitting of the initial 10 % of the reactions. Pseudo-first-order rate constants k_{obs} were calculated by fitting the experimental reaction profiles to exponentials. The toluene vapor pressure at the temperature of the system was considered in calculating dioxygen partial pressures.[16].

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[12] Crystal data for **2**$\cdot 3\,C_7H_8$: $C_{40}H_{44}N_6O_2Rh_2\cdot 3\,C_7H_8$, $M_r = 1123.04$, prismatic crystal ($0.16\times 0.05\times 0.05$ mm), triclinic, space group $P\bar{1}$, $a = 9.7616(11)$, $b = 11.5598(13)$, $c = 12.4273(14)$ Å, $\alpha = 86.458(2)$, $\beta = 68.865(2)$, $\gamma = 87.552(2)°$, $V = 1305.2(3)$ Å^{-3}, $Z = 1$, $\rho_{calcd} = 1.429\,g\,cm^{-3}$, $F(000) = 582.0$, $T = 100(2)$ K, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å, $\mu = 0.682\,mm^{-1}$). Data collected with a Bruker SMART APEX CCD diffractometer. Of 15557 measured reflections (2θ: 3.5–55°, ω scans 0.3°), 5903 were unique ($R_{int} = 0.0406$); a multiscan absorption correction was applied (SADABS program) with min./max. transmission factors of 0.932/0.955. Structure solved by Patterson and difference-Fourier maps; refined using SHELXTL. A disordered toluene molecule was found in the asymmetric unit. Final agreement factors were $R1 = 0.0506$ (5226 obs. reflections, $F^2 > 4\sigma(F^2)$) and $wR2 = 0.1086$; data/restrains/parameters 5903/0/454; GOF = 1.112. CCDC-258836 (**2**) and CCDC-258837 (**3**) 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.

[13] Crystal data for **3**: $C_{20}H_{22}N_3ORh$, $M_r = 423.31$, monoclinic, space group $P2_1/n$, $a = 10.7068(11)$, $b = 16.5017(18)$, $c = 40.470(4)$ Å, $\beta = 95.299(2)°$, $V = 7119.7(13)$ Å^{-3}, $Z = 16$, $\rho_{calcd} = 1.580\,g\,cm^{-3}$, $F(000) = 3456$, $T = 100(2)$ K, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å, $\mu = 0.972\,mm^{-1}$). Data collected as described for **2** with an irregular prism ($0.084\times 0.054\times 0.054$ mm). Of 38220 measured reflections (2θ: 2–50°), 12544 were unique ($R_{int} = 0.1048$); a multiscan absorption correction was performed (SADABS program) with min./max. transmission factors of 0.923/0.942. Structure solution and refinement as described for **2**. Two independent, but chemically equivalent, dimeric complexes were found in the asymmetric unit. Final agreement factors were $R1 = 0.068$ (6315 observed reflections) and $wR2 = 0.1737$. Data/restrains/parameters 12544/42/901; GOF = 0.998. All residual peaks above 1 e Å^{-3} were found in close proximity to the rhodium metal and have no chemical sense.

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