Ligand-Controlled Formation of a Low-Valent Pincer Rhodium(I)–Dioxygen Adduct Bearing a Very Short O–O Bond

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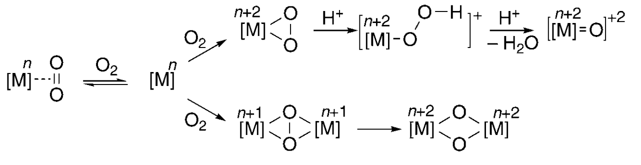
This paper is dedicated to a good friend *Gianni Consiglio* on the occasion of his retirement and in recognition of his important contributions to chemistry

Treatment of $[\{Me_2C_6H(CH_2P^tBu_2)_2\}Rh(\eta^1\text{-}N_2)]$ (**1a**) with molecular oxygen (O_2) resulted in almost quantitative formation of the dioxygen adduct $[\{Me_2C_6H(CH_2P^tBu_2)_2\}Rh(\eta^2\text{-}O_2)]$ (**2a**). An X-ray diffraction study of **2a** revealed the shortest O–O bond reported for Rh–O_2 complexes, indicating the formation of a Rh^I–O_2 adduct, rather than a cyclic Rh^{III} η^2-peroxo complex. The coordination of the O_2 ligand in **2a** was shown to be reversible. Treatment of **2a** with CO gas yielded almost quantitatively the corresponding carbonyl complex $[\{Me_2C_6H(CH_2P^tBu_2)_2\}Rh(CO)]$ (**3a**). Surprisingly, treatment of the structurally very similar pincer complex $[\{C_6H_3(CH_2P^iPr_2)_2)\}Rh(\eta^1\text{-}N_2)]$ (**1b**) with O_2 led to partial decomposition, with no dioxygen adduct being observed.

Introduction. – Oxygenation reactions with molecular oxygen (O_2) as an oxidant are of much importance in both homogeneous catalysis and metabolic systems, and are of much fundamental mechanistic interest [1–6]. Of potential significance in this regard are transition-metal complexes of dioxygen, which might be involved in such oxygenation processes. It is, therefore, essential for the understanding of reaction mechanisms and for the potential discovery of new processes to study the chemical and structural properties of metal–O_2 adducts in general. For instance, the oxidative addition of dioxygen to low-valent transition-metal complexes often leads to cyclic η^2-peroxo intermediates, which are normally nucleophilic. Oxygenating reagents, however, should be essentially electrophilic because these processes are always accompanied by the transfer of electrons from the substrate to the oxidant derived from the dioxygen adducts. Due to the deactivation of dioxygen upon oxidative addition to transition-metal centers, such intermediates are often inactive in oxygenation reactions and require activation to convert the nucleophilic peroxide species into electrophilic and reactive systems (*Scheme 1*).

Activation of mononuclear peroxo complexes could be achieved *via* protonation to yield hydroperoxo intermediates, which can be converted further by protonation into highly electrophilic oxo complexes by heterolytic O–O bond cleavage and elimination of H_2O. Such activation mechanisms have been proposed for metalloporphyrins including hemoproteins [7][8]. Other paths involve the oxidative addition of O_2 at two metal

Scheme 1. *Activation Paths Involving Transition-Metal Complexes of Dioxygen*



centers leading to nucleophilic dinuclear intermediates, which could be converted into bis(μ-oxo) species *via* O–O homolysis. Some alkane hydroxylases such as methane monooxygenase contain dinuclear bis(μ-oxo) cores in their active sites [9–13].

Despite the enormous potential of using molecular O_2 in transition-metal-catalyzed oxygenation reactions [14], most industrial processes are based on reduced forms of dioxygen, *e.g.*, peroxides, as well as catalysts with metal centers in high oxidation states [15]. By contrast, metal centers of biological systems operating with dioxygen as oxidant are usually found in low oxidation states, typically with d^6 configuration [16]. Since several natural systems are based on the heme ferryl moiety, much effort has been directed toward developing biomimetic catalytic systems based on iron porphyrin complexes [17].

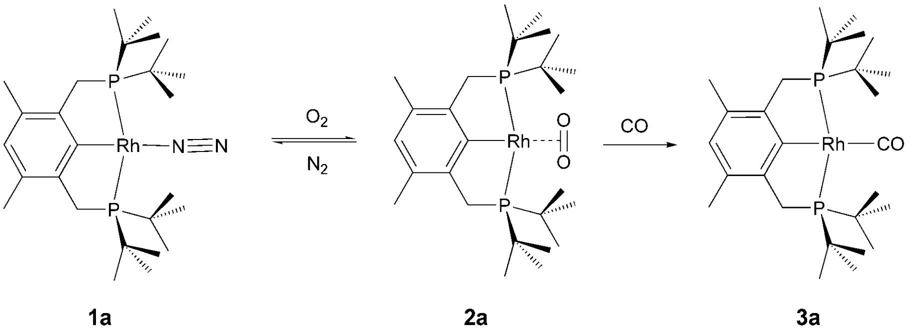
While much interest in fixation of gaseous O_2 by transition-metal complexes is motivated by the potential application in oxygenation catalysis, there is also another direction of research, namely O_2 transport, as is well-known for heme and non-heme iron complexes in nature [18]. The O_2 transport in mammals is primarily a function of erythrocyte-contained hemoglobin. The heme-iron moiety of the hemoglobin molecule allows to bind up to four molecules of O_2 within the binding pockets in each protein subunit. Interestingly, hemoglobin–O_2 interactions result in significant structural conformational changes to facilitate loading and release of O_2, respectively. Thereby, O_2 uptake is dependent upon the partial O_2 pressure to which the hemoglobin is exposed.

The most-important property of metabolic as well as artificial O_2 carriers is the fully reversible 1:1 uptake and release of O_2. Complexes capable of reversibly binding molecular O_2, leading to well-characterized dioxygen complexes, are well-known [19]. For instance, *Vaska* discovered that the iridium(I) complex $[Ir(CO)(Cl)(Ph_3P)_2]$ reversibly binds O_2 to yield $[Ir(CO)(Cl)(O_2)(Ph_3P)_2]$ [20]. Examples involving other metals have been reported, indicating the possibility to mimic metabolic O_2 carriers with essential and non-essential metal centers of structurally very simple systems [19][21]. However, the formation, structural properties, and reactivity of dioxygen complexes is not always predictable, and additional understanding is required.

Pincer complexes have attracted much interest in recent years. They have found applications in bond activation, stabilization of unusual structures, a variety of catalytic processes, and the design of functional materials [22]. Such complexes can generate relatively stable, coordinatively unsaturated species, and reversibly bind unsaturated molecules [22]. For example, we have reported that PCP-type Rh^I complexes bearing bulky alkylphosphine donor ligands reversibly bind H_2, ethene, N_2, and CO_2, allowing the determination of the relative binding affinities of these molecules [23]. We now report the synthesis and characterization (including an X-ray crystal structure) of a low-valent rhodium (Rh)–dioxygen complex. It appears that this compound has the shortest ever reported O–O bond for Rh–O_2 complexes. Accordingly, it binds O_2 reversibly, indicating its ability to function as an O_2 carrier. We have also observed a major influence of seemingly very similar ligands on the ability to form a complex with O_2.

Results and Discussion. – When O_2 was bubbled at room temperature through a benzene solution of the pincer-based dinitrogen complex $[\{Me_2C_6H(CH_2P^tBu_2)_2\}Rh(\eta^1\text{-}N_2)]$ (**1a**) [24], quantitative and instant formation of the O_2 complex $[\{Me_2C_6H(CH_2P^tBu_2)_2\}Rh(\eta^2\text{-}O_2)]$ (**2a**) was observed, accompanied by a color change from brown to deep green (*Scheme 2*). Interestingly, the $^{31}P\{^1H\}$-NMR spectrum of **2a** gave rise to a *doublet* at δ(P) 65.98 (J(P,H) = 145.6 Hz), the high coupling constant suggesting that there was formally no change in the Rh^I oxidation state [24][25]. This observation indicates low electron back-donation from the metal center into the π^* orbital of the O_2 ligand, suggesting the formation of an η^2-type Rh^I–O_2 adduct rather than that of a cyclic η^2-type Rh^{III} peroxo complex.

Scheme 2. *Reactivity of* **1a** *toward* O_2, *and of* **2a** *toward both CO and* N_2



Formation of a side-on coordinated O_2–metal complex was fully supported by the ^1H- and the $^{13}C\{^1H\}$-NMR spectroscopic data, indicating C_{2v} symmetry of the Rh center. For instance, in the ^1H-NMR spectrum, all the Me groups of the *t*-Bu units exhibit only one resonance, as found also for the Me and the CH_2 moieties of the pincer unit, showing that the structure of the complex is highly symmetric. The ^{13}C-NMR resonance at δ(C) 168.87 (*dt*, J(P,C) = 45.5, 12.8 Hz) is due to the σ-bonded aryl unit and confirms the structural integrity of the pincer core.

An X-ray diffraction study (*Fig.*) was performed with single crystals of **2a** to confirm both the formation of the complex and the proposed coordination mode of the O_2 unit. Suitable crystals were obtained by slow evaporation of a concentrated acetone solution at −30°. Important bond distances and bond angles are collected in *Table 1*.

The C(1)–Rh(1)–P(2) and C(1)–Rh(1)–P(2a) angles of 82.97(7)°, combined with the P(2)–Rh–P(2a) angle of 165.39(15)°, indicate a T-shaped Rh core for **2a**, as expected. The Rh(1)–C(1) bond distance of 2.026(15) Å compares well with similar pincer systems, where bond distances of *ca.* 2.04 Å were found [26]. When the O_2 unit is viewed as occupying a single coordination site (note that the O(1)–Rh(1)–O(1a) angle is only 39.3(5)°), then the coordination geometry around the Rh center in **2a** is distorted square-planar. Interestingly, the O–O distance is very short

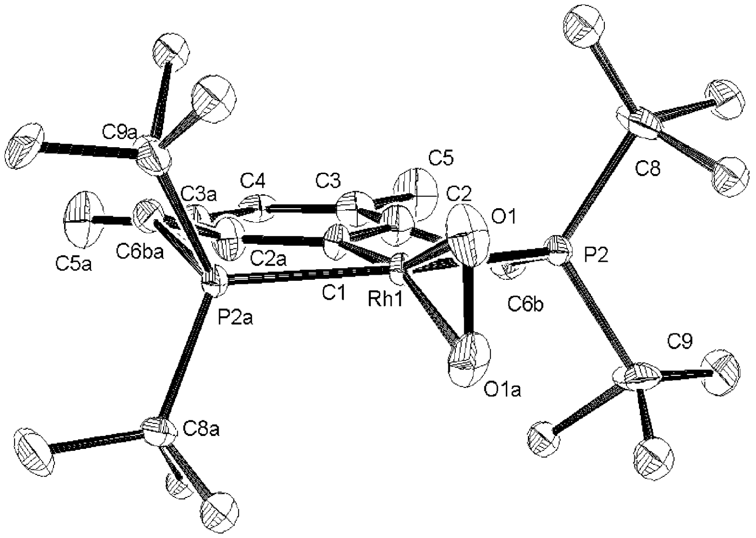


Figure. *X-Ray crystal structure of* **2a** (ORTEP representation at 20% probability). H-Atoms and split-disordered atoms of C(6) and the *t*-Bu groups are omitted for clarity.

Table 1. *Selected Bond Lengths* (in Å) *and Angles* (in °) *for* **2a**

Rh(1)–O(1)	2.030(8)	P(2)–C(6ba)	1.897(17)
Rh(1)–P(2)	2.3123(16)	C(1)–C(2)	1.424(12)
Rh(1)–C(1)	2.026(15)	C(2)–C(6b)	1.572(19)
P(2)–C(8)	1.841(9)	C(3)–C(4)	1.360(11)
P(2)–C(6b)	1.894(19)	C(4)–C(3a)	1.360(11)
C(2)–C(3)	1.411(13)	C(2a)–C(1)	1.424(12)
C(2)–C(6a)	1.572(19)	C(2a)–C(6b)	1.572(19)
C(3)–C(5)	1.504(12)	O(1)–O(1a)	1.365(18)
C(3a)–C(2a)	1.411(13)	P(2)–Rh(1)–P(2a)	165.93(15)
C(2a)–C(6ba)	1.572(19)	C(1)–Rh(1)–P(2a)	82.97(7)
Rh(1)–O(1a)	2.030(8)	C(1)–Rh(1)–P(2)	82.97(7)
Rh(1)–P(2a)	2.3123(16)	O(1)–Rh(1)–O(1a)	39.3(5)
P(2)–C(9)	1.832(9)		

(1.365(18) Å) and can definitely not be ascribed to a peroxo formulation, mean distances of *ca.* 1.48 Å being usually quoted for this functionality [27]. The short O–O bond distance in **2a** is, indeed, even much smaller than those reported for the few other crystallographically characterized Rh–O_2 complexes with side-on coordination modes (*Table 2*) [27–37].

Interestingly, there are relatively few O_2 complexes known with O–O bond distances of *ca.* 1.36 Å. In addition, most of them are early transition metals in high oxidation states, unable to donate high electron densities into the antibonding orbitals of O_2 [38]. O–O Bond distances of similar length with respect to **2a** have been found in the following late-transition-metal complexes: [Ru(C_2Ph)(O_2)(PPh_3)(Cp*)] [39], [Cp*Ru-(NiN_2S_2)(O_2)][OTf] [40], [RuCl(NO)(O_2)(PPh_3)$_2$] [41], [Ru(C_5Me_5)(O_2)(dippe)]-

Table 2. *Selected O–O Bond Distances in Crystallographically Characterized Rhodium–Dioxygen Complexes*

Complex	O–O [Å]	Ref.
$[Rh(Cl)(O_2)(PPh_3)_2]_2$	1.44(1)	[28]
$[Rh(Cl)(O_2)(PPh_3)_3]$	1.413(9)	[29]
$[Rh(O_2)(P(CH_3)Ph_2)_4][B(Ph)_4]$	1.43(1)	[30]
$[Rh(H)\{CH_2{=}C(CH_2CH_2P^tBu_2)_2\}(O_2)]$	1.434(3)	[31]
$[Rh(SPh)(O_2)(PMe_3)_3]$	1.456(6)	[32]
$[Rh(O_2)(As(CH_3)_2Ph_2)_4][ClO_4]$	1.46(2)	[33]
$[Rh(O_2)(dppe)_2][PF_6]$	1.418(11)	[34]
$[Rh(O_2)L_2][PF_6]$[a]	1.412(7)	[35]
$[\kappa^2\text{-}Tp^{Me2}Rh(O_2)(PEt_3)_2]$[b]	1.466(8)	[36]
$[\kappa^3\text{-}Tp^{Me2}Rh(O_2)(PEt_3)]$[b]	1.448	[37]

[a] L = (*R*)-1-Dimethylphosphanyl)-2-(diphenylphosphanyl)ferrocene. [b] Tp^{Me2} = tris(3,5-dimethyl-1-pyrazol-1-yl)hydroborate.

$[BPh_4]$ [42], $[OsCl(O_2)(dcpe)_2]^+$ (dcpe = 1,2-bis(dicyclohexylphosphino)ethane) [43], $[\{Cp(OC)_3W\}C{\equiv}CC{\equiv}C\{Ir(CO)(PPh_3)_2(O_2)\}]$ [44], $[Pd(O_2)(PPh^tBu_2)]$ [45], $[Ir(CO)(O_2)(PPh_3)_2(X)]$ (X = Cl [20][46], Br [47]). In these compounds, the O–O distances were in the range of 1.30 to 1.37 Å.

The weak binding of O_2 to the pincer Rh(I) complex **2a** might be a result of the strong *trans* influence of the *ipso*-C-atom of the aromatic anchor. The importance of the *trans* effect in pincer systems has been recently noted based on experimental and computational comparison of PNP and PCP Ir^{III} systems [48].

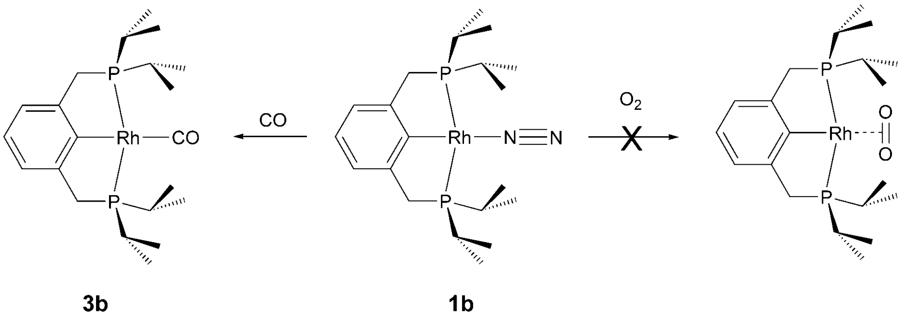
Since a relatively weak interaction of the metal center with the O_2 unit was found in **2a**, we expected that elimination of O_2 would occur under relatively mild conditions. Indeed, when **2a** was heated at 70° under N_2 atmosphere, the formation of **1a** (*ca.* 60%) and of two unidentified side products was observed. A clean conversion of **2a** was obtained when the complex was treated with an excess of CO gas, resulting in the instant and quantitative formation of the Rh–CO complex $[\{Me_2C_6H(CH_2P^tBu_2)_2\}Rh(CO)]$ (**3a**). The $^{31}P\{^1H\}$-NMR Spectrum of **3a** revealed a resonance at δ(P) 91.98 (*d*, *J*(Rh,P) = 146.35 Hz). The $^{13}C\{^1H\}$-NMR Spectrum exhibited resonances due to the CO ligand and the σ-bonded aryl unit at δ(C) 201.34 and 180.82, respectively, with *doublet*-of-*triplet* patterns and coupling constants of 55.4 and 12.6 Hz, and of 30.3 and 6.4 Hz, respectively. The IR spectrum showed a strong band at 1929 cm^{-1} due to the CO unit. The corresponding CO absorption of the very similar i-Pr congener $[\{C_6H_3(CH_2P^iPr_2)_2\}Rh(CO)]$ (**3b**) appeared at 1943 cm^{-1}, indicating a somewhat lower electron density at the metal center relative to **3a** [49]. This observation will become relevant in the following discussion.

The described reactivity of **2a** toward CO gas is in sharp contrast to that observed for the Ir–O_2 complexes $[RIr(O_2)(CO)L_2]$ (R = Me, Ph, Np; L = Ph_3P, (*p*-tolyl)$_3$P, $Me(Ph_2)P$, (*p*-$MeOC_6H_4$)$_3$P) [50]. These complexes are capable of oxidizing CO to CO_3^{2-} (carbonate), SO_2 to SO_4^{2-} (sulfate), CO_2 to peroxycarbonate, and Ph_3P to $Ph_3P{=}O$ [51]. Another interesting literature example includes the oxidation of SO_2 to SO_4^{2-} by the complex $[Ir(C_7H_4NS_2)(O_2)(CO)(Ph_3P)_2]$ ($C_7H_4NS_2$ = benzothiazole-2-

thiolate), where, additionally, incorporation of the CO group into the benzothiazole-2-thiolate ligand was observed [52]. The poor reactivity of the O_2 ligand in **2a** towards CO is compatible with its expected low nucleophilicity, as compared with peroxo-type O_2 ligands.

Remarkably, when the complex $[\{C_6H_3(CH_2P^iPr_2)_2\}Rh(\eta^1\text{-}N_2)]$ (**1b**) [53], which is structurally very similar to **1a**, was treated with molecular O_2, only partial decomposition was observed, but no formation of the corresponding Rh–O_2 complex (*Scheme 3*). This indicates a strong influence of the electron density at the metal center on its ability to bind molecular O_2. Apparently, only slight differences in electron density on the metal centers of these two derivatives, as indicated by a comparison of the corresponding carbonyl derivatives (*vide supra*), is enough for the apparent inability of **1b** to form an O_2 adduct, while, in the case of **1a**, a stable Rh–O_2 complex can be isolated.

Scheme 3. *Reactivity of* **1b** *toward CO* vs. *O_2*. No O_2 adduct was observed.



Conclusions. – We have prepared and structurally characterized a new pincer-type dioxygen Rh complex (**2a**) bearing the shortest O–O bond within the family of known, crystallographically characterized Rh–O_2 complexes, and among the shortest O–O bond for metal–O_2 complexes in general. The O_2 ligand can be readily displaced by N_2 upon heating, or by exposure to CO at room temperature. In addition, a seemingly minor structural change in the organic ligand has a dramatic effect on the ability of the complex to bind O_2. The potential application of this type of pincer complexes for the transport of O_2 is currently being explored.

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Experimental Part

General. All synthetic operations were carried out in oven-dried glassware under an atmosphere of purified N_2 in a *Vacuum Atmospheres* glove box equipped with a *MO 40-2* inert-gas purifier. Solvents were reagent grade or better, and were dried, distilled, and degassed before introduction into the glove box, where they where stored over activated 4-Å molecular sieves. Deuterated solvents were purchased from *Aldrich*, and were degassed and stored over activated 4-Å molecular sieves in the glove box. All commercially available chemicals were used as received. IR Spectroscopic data are reported in cm^{-1}.

^{1}H-, ^{13}C{^{1}H}-, and ^{31}P{^{1}H}-NMR Data were recorded at 500.13, 125.76, and 202.46 MHz, resp., on *Bruker AMX-500* and a *DPX-250* spectrometers; chemical shifts δ in ppm, coupling constants J in Hz. The ^{1}H- and ^{13}C-NMR chemical shifts are reported rel. to Me_4Si (=0 ppm); the resonance of the residual H-atoms of the solvents were used as internal standard for ^{1}H-NMR (benzene: δ(H) 7.15, δ(C) 128.0). ^{31}P-NMR Chemical shifts are reported downfield rel. to external 85% H_3PO_4 in D_2O at δ(C) 0.0. All measurements were carried out at 298 K. NMR Abbreviations: *s*, *singlet*; *d*, *duplet*; *t*, *triplet*. Elemental analyses were performed by *H. Kolbe*, Mikroanalytisches Laboratorium, Germany.

Preparation of $[\{Me_2C_6H(CH_2P^tBu_2)_2\}Rh(\eta^2\text{-}O_2)]$ (**2a**). Molecular O_2 was bubbled through a soln. of $[\{Me_2C_6H(CH_2{}^tBu_2)_2\}Rh(N_2)]$ (**1a**) [24] (15 mg, 27 µmol) in benzene (5 ml) for 1 min, which resulted in an immediate color change from yellow to dark green. Evaporation of the solvent under reduced pressure gave **2a** as a green powder in quant. yield. ^{1}H-NMR: 6.76 (*s*, arom. H); 4.43 (*t*-like, J=3.7, 2 CH_2P); 2.22 (*s*, 2 Me); 1.45 (*t*-like, J=6.1, 4 *t*-Bu). ^{13}C{^{1}H}-NMR: 168.87 (*dt*, J=45.5, 12.8, C_{ipso}); 152.75 (*dt*, J=13.2, 9.5, arom. C); 133.05 (*s*, arom. C); 129.00 (*dt*, J=12.8, 9.6, arom. C); 35.32 (*dt*, J=12.8, 6.4, Me_3C); 34.02 (*dt*, J=12.8, 6.3, CH_2P); 30.37 (*s*, Me_3C); 22.40 (*s*, Me). ^{31}P{^{1}H}-NMR (C_6D_6): 65.98 (*d*, J(Rh,P)=145.6). Anal. calc. for $C_{26}H_{47}P_2O_2Rh$: C 56.11, H 8.51; found C 55.93, H 8.45.

Reaction of **2a** *with* N_2. When a benzene soln. of **2a** was heated at 70° for 3 h, the formation of **1a** (*ca.* 60%), along with other decomposition products, was observed spectroscopically.

Preparation of $[\{Me_2C_6H(CH_2P^tBu_2)_2\}Rh(CO)]$ (**3a**). Gaseous CO was bubbled through a benzene soln. (5 ml) of **2a** (20 mg, 3.5 µmol) for several minutes. An immediate reaction took place, accompanied by a color change from green to yellow. Removal of the solvent under reduced pressure yielded **3a** as a yellow solid. Yield: 19.8 mg (>98%). IR (film): 1929 (*s*, C=O). ^{1}H-NMR: 6.74 (*s*, arom. H); 3.31 (*t*-like,

Table 3. *Crystallographic Data for* **2a**

Formula		$C_{26}H_{47}O_2P_2Rh$
M_r [g/mol]		556.49
Crystal habit, color		prism, black
Crystal size [mm]		0.2×0.2×0.1
T [K]		120(2)
Crystal system		Tetragonal
Space group		$P4_2$
Lattice parameters:	a [Å]	11.5590(16)
	b [Å]	11.5590(16)
	c [Å]	10.298(2)
Z		2
V [Å^3]		1375.9(4)
$D_{calc.}$ [g/cm^3]		1.616
μ [mm^{-1}]		0.756
F(000)		588
θ [°]		2.65–27.44
Scan type		Φ
λ [Å]		0.71073
Total reflections collected		20834
Reflections used in refinement		1630
Reflections with $I>2\sigma(I)$		1304
Parameters refined		158
Restraints		1
$R1(F)$, $wR2$ ($I>2\sigma(I)$)[a]		0.0451, 0.1235
$R1(F)$, $wR2$ (all data)		0.0637, 0.1328
Goodness-of-fit		1.024
$\Delta\rho$ (min; max) [e/Å^3]		−1.035, 0.646

[a] $w=1/[\sigma^2(F_o^2)+(0.0830P)^2+1.81173P]$.

$J=3.7$, 2 CH_2P); 2.29 (*s*, 2 Me); 1.28 (*t*-like, $J=6.1$, 4 *t*-Bu). $^{13}C\{^1H\}$-NMR: 201.34 (*dt*-like, $J=55.4$, 12.6, CO); 180.82 (*dt*-like, $J=30.3$, 6.4, C_{ipso}); 150.08 (*td*-like, $J=12.2$, 2.9, C_{ipso}); 129.50 (*s*, arom. C); 128.65 (*td*-like, $J=6.1$, 6.1, arom. C); 36.39 (*td*-like, $J=10.6$, 2.3, Me_3C); 35.16 (*t*-like, $J=7.4$, CH_2P); 29.91 (*t*-like, $J=3.2$, Me_3C); 22.81 (*s*, Me). $^{31}P\{1H\}$-NMR (C_6D_6): 91.98 (*d*, J(Rh,P)$=146.35$). Anal. calc. for $C_{27}H_{47}P_2ORh$: C 58.69, H 8.57; found: C 58.93, H 8.45.

X-Ray Crystal-Structure Determination of **2a**. All measurements were performed on *a Nonius Kappa CCD* diffractometer using graphite-monochromated MoK_α radiation ($\lambda=0.71073$ Å). The data-collection and refinement parameters are given in *Table 3*, and views of the molecules are shown in the *Figure*. The data were processed with Denzo-Scalepack. The structure was solved by direct methods with SHELXS-97 [54]. The refinement of the structure was carried out on F^2 using full-matrix least-squares with SHELXL-97 [55]. The crystallographic data of **2a** have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication number CCDC-604230. Copies of the data can be obtained at http://www.ccdc.cam.ac.uk/data_request/cif.

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