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DOI
10.1002/chem.202000387

Publication date
2020

Document Version
Final published version

Published in
Chemistry-A European Journal

License
Article 25fa Dutch Copyright Act

Citation for published version (APA):
Electron-Deficient Compounds

Three-Coordinate Rhodium Complexes in Low Oxidation States

Victor Varela-Izquierdo,[a] José A. López,[a] Bas de Bruin,[b] Cristina Tejel,*[a] and Miguel A. Ciriano*[a]

Abstract: The isolation of simultaneously low-coordinate and low-valent compounds is a timeless challenge for preparative chemists. This work showcases the preparation and full characterization of tri-coordinate rhodium(-I) and rhodium(0) complexes as well as a rare rhodium(I) complex. Reduction of [(Rh(µ-Cl)(IPr)(dvtms))] ([1, IPR = 1,3-bis(2,6-diisopropylphenyl)imidazolyl-2-ylidene; dvtms = divinyltetramethyldisiloxane)] with KCl gave the trigonal complexes [Rh(IPr)(dvtms)] and [Rh(IPr)(dvtms)], whereas the cation [Rh(IPr)(dvtms)]+ results from their oxidation or by abstraction of chloride from 1 with silver salts. The paramagnetic Rh3 complex is a unique fully metal-centered radical with the unpaired electron in the d2 orbital. The Rh(-I) complex reacts with PPh3 with replacement of the NHC ligand, and behaves as a nucleophile, which upon reaction with [AuCl(PPh3)] generates the trigonal pyramidal complex [[IPr(dvtms)Rh-Au(PPh3)] with a metal–metal bond between two d10 metal centers.

Low-valent transition-metal complexes that simultaneously have low coordination numbers are highly reactive species, which have been proposed as intermediates in transition-metal catalyzed reactions.[1] This class of compounds can mediate chemical bond activations and are a source of unusual compounds with new electronic properties. From a synthetic point of view, the stabilization of metal atoms in low oxidation states and with low coordination numbers has been a challenging target for decades. Typically, carbon monoxide, olefins, and phosphines have been utilized to stabilize low-valent metal compounds. Despite their much higher σ-donation properties (NHC→M), NHC ligands have favorably replaced phosphine ligands for this purpose, taking advantage of their bulkiness.[2] Thus, zero-valent low-coordinate palladium and platinum complexes with NHCs are well-known compounds[3] and there are quite a few complexes of the first-row transition metals of this type.[4] However, to date low oxidation state rhodium(0) or rhodium(-I) compounds with NHC ligands have remained unreported.

Rh5 and Rh(-I) compounds have been known for 50 years. Many of them were electrochemically generated as short-lived intermediates,[5] or isolated as complexes with strong σ-acceptor ligands such as [Rh(CO)]3− or [Rh(F3P)3]−, and as polynuclear clusters.[6] Afterwards, fully characterized d2-ML4 and d10-ML4 compounds with diphenylphosphine,[7] and mixed olefin-phosphine ligands have been reported and extensively studied by Grützmacher (Scheme 1).[8] They are typically tetracordinate, thus following the 18-electron rule, and display more or less distorted tetrahedral structures, except the distinctive trigonal pyramidal [K(thf)][P2-Rh] [P2-Rh = tris(diisopropylphosphine-phenyl)-silyl].[9] Those of Rh3 have been characterized and many of them fully studied by EPR spectroscopy and DFT methods.[10] Interestingly, they are all highly delocalized radicals, with the exception of one metal-centered radical, [Rh(trop,PPh)(PPh3)], [p(Rh) 58%], which is in electrochemical equilibrium with the delocalized radical.[11] In any case, isolated compounds of rhodium in the oxidation states 0 and −1 are rare and their chemistry is underdeveloped.

Regarding this general panorama, we decided to explore reduction reactions of NHC rhodium complexes to confirm if electron-rich metal centers are compatible with strong σ-donor ligands in the coordination sphere of rhodium. Herein, we describe the preparation and properties of the first isolated NHC rhodium(0) and rhodium(-I) complexes, which are unique examples of low-valent and low-coordinate rhodium complexes in a trigonal planar environment, and some of their reactions. The election of the ancillary ligands is crucial for stabilizing the products. For example, reduction of [RhCl(IPr)(cod)] (IPR =

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[a] V. Varela-Izquierdo, Dr. J. A. López, Dr. C. Tejel, Prof. Dr. M. A. Ciriano
Departamento de Química Inorgánica
Instituto de Síntesis Química y Catalisis Homogénea (ISQCH), CSIC
Universidad de Zaragoza
Pedro Cerbuna 12, 50009 Zaragoza (Spain)
E-mail:ctejel@unizar.es
mciriano@unizar.es

[b] Prof. Dr. B. de Bruin
Van’t Hoff Institute for Molecular Sciences
University of Amsterdam
Science Park 904, 1098 XH Amsterdam (The Netherlands)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
https://doi.org/10.1002/chem.202000387.


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1,3-bis(2,6-diisopropylphenyl)imidazolyl-2-ylidine; cod = 1,5-cyclooctadiene with KC₈ in THF does occur, but the intermediate species undergoes further transformations that will be reported elsewhere. We only succeed in isolation of the primary reduced species when using an open and more adaptable chelating diolene than cod, such as divinyltetramethylsilisoxane (dvtems). The precursor complex [Rh(μ-Cl)(IPr)(dvtems)] (1) was prepared and characterized by X-ray and conventional methods. Complex 1 is dinuclear with two chloride bridges, the diolene coordinated by only one vinyl η²-C=C bond, and the NHC ligands in a transoid disposition. The complex is fluxional in solution, but the low-temperature NMR spectra are consistent with the structure found in the solid state. For comparative purposes, the NMR chemical shifts and C=C bond distances of the coordinated and non-coordinated ligand double bonds are presented in Table S1 (Supporting Information).

Reduction of 1 with KC₈ in THF takes place in two steps to give first [Rh(IPr)(dvtems)] (2), and then K[Rh(Pr)(dvtems)] K[2] (Scheme 2). Additionally, disproportionation of K[2] with 1 in THF occurs to give 2 immediately, providing thus a second method to isolate 2 cleanly. A similar disproportionation reaction to 2 was observed by reacting K[Rh(IPr)(dvtems)] (K[2]) with [Rh(Pr)(dvtems)]PF₆ (2PF₆) (see below).

Complexes 2 and K[2] were isolated as very sensitive to oxygen and moisture crystalline brown-orange solids after workup. Their X-ray structures (Figure 1) revealed they are trigonal-planar complexes with the metals bound to the NHC ligand and to dvtems through both C=C bonds with all the carbon atoms virtually in the molecular plane.

This feature contrasts with the C=C bond coordination perpendicular to the molecular plane of olefins in square-planar Rh complexes. The “planar” disposition leads to strong shifts with KC₈ and square-planar Rh in solution, but the low-temperature NMR spectra are consistent with the structure found in the solid state. For comparative purposes, the NMR chemical shifts and C=C bond distances of the coordinated and non-coordinated ligand double bonds are presented in Table S1 (Supporting Information).

Figure 1. Molecular structure (ORTEP, ellipsoids set at 50% probability) of complexes [Rh(IPr)(dvtems)] (2) (left) and K[Rh(IPr)(dvtems)] K[2] (right). Selected bond distances [Å] and angles [°] for 2: Rh–C1 2.092(3), Rh–C1t 2.024(4), Rh–Ct1 2.030(4), C28–C29 1.422(6), C32–C33 1.421(6), C1–Rh–Ct1 111.2(2), C1–Rh–Ct2 117.3(2), C1t1–Rh–Ct2 130.6(2); for K[2]: Rh–C1 2.0363(13), Rh–Ct1 1.990(4), Rh–Ct2 1.989(1), C28–C29 1.435(2), C32–C33 1.436(2), C1–Rh–Ct1 112.3(1), C1–Rh–Ct2 111.7(1), C1t1–Rh–Ct2 135.9(1). C1t and Ct2 are middle points of C28, 29 and C32, 33, respectively. Only CH carbons of the IPr groups are shown for clarity.

Complexes 2 and K[2] were isolated as very sensitive to oxygen and moisture crystalline brown-orange solids after workup. Their X-ray structures (Figure 1) revealed they are trigonal-planar complexes with the metals bound to the NHC ligand and to dvtems through both C=C bonds with all the carbon atoms virtually in the molecular plane.

The diamagnetic complex K[2] maintains in solution the structure found in the solid state, although a more symmetric averaged molecule is observed by NMR spectroscopy due to the free rotation of the phenyl groups and the imidazolyl-2-ylidine ring around the C–N and C–Rh bonds, respectively. The shift to high field of the vinyl protons and carbons that appear in the aliphatic region is noticeable and in agreement with strong π-back donation (Table S1, Supporting Information). In addition, the carbene carbon is observed at low field and shifted up to ca. 60 ppm relative to complex 1.

The Rh² complex 2 is paramagnetic. The magnetic moment (1.7 μB, Evans’ method) is in agreement with an S = 1/2 ground state with one unpaired electron. It shows broad signals in the ¹H NMR spectrum, in the range between δ = −10 and 110 ppm. The EPR spectrum of 2 (Figure 2, left) reveals a rhombic (nearly axial) g-tensor with large g-anisotropy. A satisfactory simulation was obtained using the parameters shown in Table 1. The large deviations of the g-values from gₐ and the relatively large Rh hyperfine couplings (well-resolved along gₐ) show that the unpaired electron of complex 2 resides in a mainly metal-centered SOMO. This was confirmed by supporting DFT calculations, showing that the unpaired electron of 2 resides predominantly in the metal dₐ orbital (Figure 2, right).

**Notes:**
- **Figure 2:** Experimental and simulated EPR spectrum of 2. Experimental parameters: Microwave frequency = 9.392888 GHz, microwave power = 0.632 mW, modulation amplitude = 2 Gauss, temperature = 10 K (left) and spin density plot of 2 showing that the unpaired electron resides almost entirely in the Rh dₐ orbital (right).
The DFT calculated EPR parameters of 2 are in good agreement with the experimental parameters (Table 1). In contrast to all the previously reported formal rhodium(0) complexes,[9,10,11] complex 2 is a genuine metal-centered radical.

Cyclic voltammetry measurements on the radical-complex 2 in thf revealed a redox couple centered at $-1.36$ V (versus SCE) corresponding to the $2^+\rightarrow 2^-$ process. The shape of this wave indicates a further irreversible chemical reaction undergone by the electrogenerated anion $2^-$ because values of $i_{pa}/i_{pc}$ were $<1$, and they increased as the scan rate does, reaching a value of 0.6 at a 500 mV s$^{-1}$. This lack of reversibility could be attributed to the adventitious presence of traces of oxygen or water that destroy the anionic complex $2^-$. A second wave, fully irreversible, in this case, was observed at $-0.1$ V, which has been assigned to the one-electron oxidation reaction of 2 to the cationic complex $2^+$. The irreversibility observed in this case is due to a change in the coordination environment of rhodium (see below).

The low potential at which complex 2 is oxidized makes feasible its chemical oxidation (also expected for $2^-$) by [CP$_3$Fe][PF$_6$. Accordingly, oxidation of K[2] with [CP$_3$Fe][PF$_6$ in thf (1:2 molar ratio) provides the orange cationic complex [Rh(IPr)(dvtms)][PF$_6$], which was isolated as a microcrystalline solid in good yield. This compound can be also prepared by abstraction of chloride from [Rh(IPr)(dvtms)][PF$_6$] by BF$_4^-$, which replaces the IPr ligand to give K[Rh(PPh$_3$)(dvtms)] (Figure 4). A confirmation of this kind of reaction is possible its chemical oxidation (also expected for $2^-$) with $\mathrm{O}_2$. A second wave, fully irreversible, in this case, was observed at $-0.1$ V, which has been assigned to the one-electron oxidation reaction of 2 to the cationic complex $2^+$. The irreversibility observed in this case is due to a change in the coordination environment of rhodium (see below).

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The structure of the cation in [2][BF$_4$] is shown in Figure 3.

The rhodium atom in $2^+$ shows a distorted square-planar environment bound to the carbon (C1) of the carbene and to a highly tensioned divinyltetramethyldisiloxane (dvtms) through both C=C bonds and the oxygen atom as a rare tridentate pincer ligand. Oxygen displays a highly distorted geometry, close to a T-shaped arrangement with a Si1-O-Si2 angle of 160.4(2)°, as can be clearly observed in Figure 3. Both C=C bonds are placed in between the “planar” orientation found in 2 and $2^-$ and the typical orthogonal disposition for rhodium(1) complexes. The C=C bond distances of 1.370(6) and 1.378(6) Å are quite shorter than in complexes 2 and $2^-$, in agreement with a smaller extension of the π-back donation expected for a Rh" center. The cation [2]$^+$ was found to be fluxional a r.t., but the $^1$H and $^{13}$C($^1$H) NMR spectra at $-50^\circ$ C (CDCl$_3$) agreed with a species having a C$_2$ symmetry axis that makes the two halves of the molecule equivalent. On raising the temperature, broad-line effects on the resonances corresponding to the aryl groups were observed. Noticeably, one can also observe the coalescence and emergence as a singlet of the methyl groups bonded to silicon, which requires the formal inversion of the oxygen atom. From the VT-$^1$H NMR spectra, the activation parameters for this process were found to be $\Delta H^\ddagger = 20.0 \pm 0.7 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = 18.2 \pm 1.1 \text{ cal mol}^{-1} \text{ K}^{-1}$. The positive value for $\Delta S^\ddagger$ evidences a more disordered transition state that has to stabilize the cleavage of the Rh–O bond. A further inversion of the six-membered metallocycle (Rh-C1-Si1-O-Si2-C2) followed by coordination of oxygen accounts for the observed dynamics. Indeed, the Rh–O bond is weak and can be easily broken down. Accordingly, the O-bound species [Rh(IPr)(dvtms)] ($2^-$) was computed to be only 9.8 kcal mol$^{-1}$ more stable than that with the dissociated O-atom.

The Rh(I) complex [K2] reacts with triphenylphosphine, which replaces the IPR ligand to give K[Rh(PPh$_3$)(dvtms)] (K[3]), a reaction opposite to the early syntheses of NHC complexes in which phosphine was changed by NHC ligands (Figure 4).[3a] Most probably the difference in the π-accepting properties of both ligands is the driving force of the reaction. The geometry

### Table 1. Experimental and DFT calculated EPR parameters of 2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Exp. (spectral simulation)</th>
<th>DFT$^{\text{DFT}}$</th>
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<td>$A_{\text{eff}}^{\text{N-Rh}}$</td>
<td>NR (220 MHz)$^{\text{II}}$</td>
<td>$-247$ MHz</td>
</tr>
</tbody>
</table>

[a] ADF, B3LYP, TZ2P, collinear unrestricted spinorbit ZORA. [b] Rhodium hyperfine interaction tensor. [c] NR = not resolved. Values between brackets are rough estimated values based on line shape analysis, assuming that the experimental line width is smaller than the Rh hyperfine interactions.
around rhodium is again trigonal-planar, bound to the phosphorus atom and to both C–C bonds, again in a "planar" orientation. The C–C bond lengths were found to be similar to those in K[2], although their NMR data exhibited a low-field shift of the signals relative to K[2] in the 1H and 13C NMR spectra. These shifts agree with a smaller extension of the π-back donation from Rh to the C–C bonds because of the better π-accepting properties of PPh3 than IPr, which on the whole stabilizes complex K[3].

Reaction of the anionic complex K[2] with [AuCl(PPh3)] gave the neutral complex ([IPr](dvtms)RhAu(PPh3)) (4) that features a metal–metal bond and a trigonal pyramidal structure with the gold atom at the apex (Figure 5).

Figure 5. Synthesis of complex ([IPr](dvtms)RhAu(PPh3)) (4) and molecular structure (ORTEP, ellipsoids set at 50% probability) of the major isomer 4a. Selected bond distances [Å] and angles [°]: Rh–Au 2.5302(3), Rh–C1 2.073(2), Rh–Ct1 2.018(2), Rh–C2 2.021(2), C28–C29 1.434(3), C32–C33 1.431(3), Au–P 2.2477(7), C1-Rh-Ct1 114.96(9), C1-Rh-C2 109.79(9), C1-Rh-C12 134.86(10), Rh-Au-P 163.13(2). C1 and C2 are middle points of C28,29 and C32,C33, respectively. Only CH carbons of the IPr groups are shown by clarity.

Complex 4 exists in solution as a mixture of two interconverting isomers 4a/4b from which the most abundant 4a (77%) is the only one found in the solid state. The main difference between these structures is the position of the Au(PPh3) fragment relative to the basal plane, as deduced by NMR methods (see Supporting Information). The topology of the basal plane is similar to that of complexes 2, [2]−, and [3]−, including the C–C bond distances. Whereas the chemical shifts of the olefinic protons in 4a/4b are low-field shifted relative to those of [2]−, the olefin 13C chemical shifts are similar to those of [3]−, which is indicative of a smaller back-donation to the olefin than in [2]−.

Complex 4 can be considered as either a covalent Rh5–Au5 complex or Rh(–I)–Au complex with a dative metal–metal bond. We favor the latter description, based on the structure and the above NMR data. Moreover, NBO-analysis showed charges on the metals to be 0.28307 (Au) 0.07809 (Rh) and a Wiberg bond index 0.60973. As such, complex 4 represents a rare complex with two interacting closed-shell d10 centers.

Both isomers 4a/4b decompose in [D8]toluene slowly and cleanly up to the half-life = 13.5 h through an exchange of the IPr and PPh3 ligands on gold and rhodium (Scheme 3).

The new complex 5 was characterized by NMR methods, which clearly indicated the coordination of the NHC to gold and the phosphine to rhodium (see Supporting Information). In particular, key data were the changes in the coupling constants J(C,Rh) and J(P,Rh) on going from 4a to 5 (see Scheme 3). Also relevant is the shift to high field of the N-C-N carbon bonded to gold (δ = 208.4 ppm in 4a, and 166.2 ppm in 5).

DFT studies on complexes 4a and 5 indicated that 5 is 14.4 kcal mol−1 more stable than 4a, which can be attributed to a smaller steric clash between the PPh3 and NHC ligands in 5. Moreover, the Rh–Au bond length was found to be slightly shorter in 5 (2.525 Å) than in 4a (2.547 Å), whereas the Wiberg bond indexes indicate a stronger Rh–Au bond in 5 (0.88811) than in 4a (0.60973). Moreover, according to the natural charges on the metals (Au, 0.34900; Rh, −0.07240) complex 5 contains a more polarized metal–metal bond.

In conclusion, we showcase the synthesis of novel and unique tri-coordinate rhodium(0) and rhodium(-I) complexes. Thus, K[Rh(IPr)(dvtms)] was isolated from the reduction of [[Rh(μ-Cl)(IPr)(dvtms)]3] with KC8, while the triphenylphosphine analogue arises from the easy ligand replacement of IPr by PPh3. One-electron reduction of the Rh complex gave the rhodium(0) complex [Rh(IPr)(dvtms)], a unique 15 VE. localized metal-centered radical. Moreover, the anionic Rh(-I) complex reacts with [AuCl(PPh3)] to give the trigonal pyramidal complex ([IPr](dvtms)Rh-Au(PPh3)), with a metal–metal bond between two d10 metal centers. Further studies on these very reactive complexes are currently in progress.

Acknowledgements

The generous financial support from MINECO/FEDER/AGE (CTQ2017-83421-P, C.T.), Gobierno de Aragón/FEDER (GA/FEDER, Inorganic Molecular Architecture Group E08_17R; C.T.) and the Netherlands Organization for Scientific Research (NWO) (TOP Grant 716.015.001, BdB) is gratefully acknowledged. V.V.-I. thanks MINECO/FEDER for a FPI fellowship.

Conflict of interest

The authors declare no conflict of interest.

Keywords: low-valent · metal–metal bond · NHC ligands · rhodium · tri-coordinate

Manuscript received: January 22, 2020
Accepted manuscript online: January 27, 2020
Version of record online: February 19, 2020